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A SURVEY ON RESEARCH POSSIBILITIES FOR ANIMAL FATS

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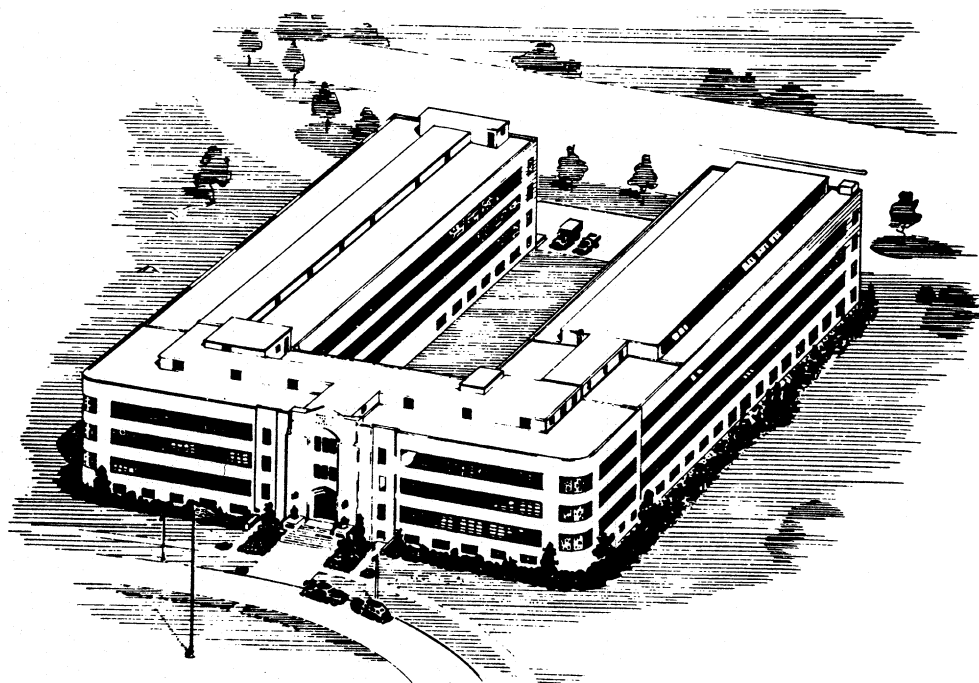
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A SURVEY ON RESEARCH POSSIBILITIES FOR ANIMAL FATS[1]

by Daniel Swern, [2] Waldo C. Ault[2] and John W. McCutcheon[3]

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INTRODUCTION

Animal fats are by-products of the livestock industry and their production cannot be readily controlled; in fact, their production continues to increase as meat production increases. The domestic consumption of animal fats has lagged far behind production for a number of years, and it was estimated early in 1950 that the surplus would be 300,000,000 to 400,000,000 pounds by the end of the year. Since the per capita consumption of edible fats is relatively inelastic, new outlets for the anticipated increasing surpluses must be found, mainly in the industrial field.

New large-scale uses for animal fats can be developed only by organized and directed research. While some research has been and is being conducted by both Governmental and industrial organizations to develop new and expanded uses for animal fats, additional and diversified research is required. To obtain information on promising fields of research, the Department of Agriculture, under authority granted it by the Research and Marketing Act of 1946 (Public Law 733, 79th Congress, 60 Stat. 1082) entered into a contract (Number A-1s-32689) on June 29, 1950 with John W. McCutcheon, a private industrial consultant of New York City, to make a survey, some of the important objects of which were (a) to obtain complete information on present uses of edible and inedible animal fats, such as lard and edible tallow and inedible tallow and grease, (b) to obtain information on present and promising fields of research on edible and inedible animal fats, (c) to evaluate major research accomplishments over the past twenty years in the field of animal fats, and (d) to make recommendations regarding the directions of present and future research programs.

It was decided that the best approach to the problem was to interview, preferably in person but also by correspondence and telephone, at least 150 individuals and/or research groups to obtain information under the various objects given in the preceding paragraph. The individuals and groups to be consulted were selected from industrial, university, government and independent research organizations. Included were producers of fatty acids and derivatives, producers and users of fats and derivatives, producers of the active ingredients of synthetic detergents, research institutes and associations connected with fats and oils, and individuals interested in the subject. The consultations were to be based broadly upon an INTERVIEW OUTLINE AND QUESTIONNAIRE which was not intended to be an inflexible instrument but was intended to indicate phases of the survey to be explored in greater detail.

Since it was believed that the best chances for reducing the surplus of animal fats by any significant quantity would result from the development of non-soap uses, the emphasis in the survey was placed on obtaining information on possible uses of animal fats and products derived from them in such important industrial applications as synthetic detergents, organic

chemicals and plastics, three of the most rapidly growing industrial chemical fields. Thus, the emphasis in the survey was about three-fourths on inedible animal fats and one-fourth on edible animal fats. Further, the major emphasis in the survey was to be on research aspects of animal fat work, although it was recognized that it would probably be impossible to dissociate this completely from market analyses and projects already in commercial production. As a rough line of division, we were primarily interested in research work up to and perhaps including the pilot plant. A companion survey was conducted by John W. McCutcheon for the Production and Marketing Administration at about the same time as the present one and emphasized the marketing possibilities for animal fats.

This survey is divided into three sections, namely, Section 1: Inedible Animal Fats, Their Purification, Separation and Chemical Modification; Section 2: Fatty acids and Derivatives; and Section 3: Edible Animal Fat Products. In addition to the SUMMARY AND MAJOR CONCLUSIONS part of this survey which appears immediately after the introduction, there are briefer and more specific summaries at the end of each main subject discussed.

The period during which the active part of the survey was conducted was from about July 1950 to September 1951.

Acknowledgment

SUMMARY AND MAJOR CONCLUSIONS

Section I

Inedible Animal Fats

Approximately 80% of all inedible tallow and grease is used in soap, 10% goes to fatty acid production and 10% to miscellaneous industrial uses. Although a definite trend toward the use of softer fats, such as grease and lard, in soap manufacturing has been noted, the total consumption compared with the total domestic disappearance has remained constant.

Increased demands for detergents has been met by synthetic detergents. It is estimated that if synthetic detergents were not available, an added 350 million pounds of inedible tallow and grease would have been required in 1949 to meet the demand. The present growth of synthetic detergents is such that a further 30 million pounds of animal fats is being displaced yearly, practically all of which is in the soap powder field. Very probably a production of 2.0 billion pounds of synthetic detergents representing a displacement of 550 million pounds of animal fat, may ultimately be reached. Although the use of animal fats in synthetic detergents is increasing, the estimated total use for this purpose will probably remain relatively small in tonnage.

Substitution reactions such as halogenation may prove of great value in increasing animal fat use in soaps or synthetic detergents.

Total fatty acid production (animal and vegetable) in 1949 was approximately 600 million pounds. An examination of fatty acid uses indicates a fertile field for investigation, particularly as any wide scale expansion would draw on the animal fats as a source of raw material. A more intensified research program on animal fats appears necessary. Various factors hinder such work, chief of which is the unstable price structure.

Research on processing methods indicates that the solvent crystallization process involving the use of propane is worth special consideration. Chemical bleaching has raised controversial points which require further elucidation.

Section 2

Fatty Acids and Derivatives

Production is largely confined to high pressure hydrolysis or the Twitchell method. This last must now be considered obsolete. Separation of animal fatty acids is largely done by solvent crystallization using acetone or an alcohol. Pressing methods are obsolete. Other methods of interest include crystallization from a non-polar solvent and separation by chromatographic means.

Of the carboxyl modified derivatives of the fatty acids the following deserve special attention from the point of view of production:

(1) The monoglycerides and ethylene oxide derivatives as emulsifiers for food.

(2) The metallic salts for use in lubricants.

(3) Substituted amides as detergents.

(4) Amine salts as non-metallic ore flotation agents.

(5) Hydrogenation of heavy metal salts to alcohols.

Research should be directed toward preparation of products not competitive with short chain products, or where the unusual properties offer an advantage.

Five types of research have been mentioned which will have a tendency to improve soap and strengthen its overall position. A few competitive non-fat petroleum derivatives have also been mentioned, the most important of which is the fatty acids prepared from ethylene and a short chain acid, such as acetic acid. The most important additive to fatty acids or its derivatives is ethylene oxide.

Internal chain modification has been considered with respect to saturated and unsaturated acids. Elaidinization is not considered promising. Addition reactions involving hydrogen are apparently the best known. Fission products of oleic yield azelaic and pelargonic acids whose derivatives are very important. Oxidation products and substitution reactions of saturated acids are important but further study is required.

Section 3

Edible Animal Fat Products

Edible tallow and lard production, with small exception, is fixed by factors beyond that of supply and demand. In normal years only a minor fraction is used for inedible purposes. The total consumption of fats is limited so that any great increased use of one fat would be made at the expense of another. Both lard and shortening have reached a dominant and stable position. The most interesting post war use of edible fats is the use of lard as a base material in shortening. Latest available data shows this use to be 6.4% of total disappearance. It is estimated that it could reach 30%.

The technical development most responsible for this new use is the addition of stabilizers. Other processing factors include deodorization, hydrogenation, packaging, and marketing. These have been solved to a point where a satisfactory product is being made. Further work suggested is (1) the development of a hydrogenation process particularly suitable for lard, (2) a clarification of the terminology involving products derived from lard.

The use of inedible animal fats as an ingredient of animal feeds has been briefly discussed.

SECTION 1

INEDIBLE ANIMAL FATS; PRODUCTION, PURIFICATION, SEPARATION AND CHEMICAL MODIFICATION

Statistics on Inedible Tallow and Grease

To obtain a proper balance as to the opportunities for expansion in the inedible animal fat and fatty acid field, it is necessary to have some understanding of the present statistics of the industry. Factory consumption of tallow and grease in soap for the period 1936 - 1949 is given below.

Table 1

CONSUMPTION OF INEDIBLE TALLOW AND GREASE IN SOAPS

1936 - 1949   (Thousands of lbs.)

A.   INEDIBLE TALLOW[1]/

Year	Total Consumption	Consumption in Soap	% of Total Consumed in Soap	Average[2]/ Price
1936	725,974	660,020	91.0	6.6
1937	675,918	613,509	90.8	8.3
1938	764,041	702.267	92.0	5.6
1939	874,099	785,041	89.9	5.5
1940	884.685	786,456	89.0	4.5
1941	1,190,542	1,057,303	88.8	7.6
1942	1,342,396	1,188.923	88.5	9.2
1943	1,081,744	896,286	82.8	8.6
1944	1,210,625	1,005,777	83.1	8.6
1945	1,210,834	952,334	78.5	8.6
1946	1,165,218	871,968	74.8	11.2
1947	1,344,636	1,108,909	82.4	19.2
1948	1,211,995	980,670	80.8	16.0
1949	1,141,420	961,505	84.3	6.3

B.   GREASE[1]/

Year	Total Consumption	Consumption in Soap	% of Total Consumed in Soap	Average[3]/ Price	Price Ratio Tallow/Grease
1936	204,532	98,714	48.3	5.7	1.16
1937	215,651	94,247	43.8	7.3	1.14
1938	182,767	96,356	52.7	4.8	1.17
1939	210,911	120,856	57.0	4.8	1.14
1940	356,513	256,886	72.1	4.0	1.13
1941	470,214	310,487	66.0	7.0	1.08
1942	517,369	338,974	65.5	8.8	1.04
1943	677,504	463,811	68.4	8.4	1.02
1944	712,089	523,972	73.5	8.4	1.02
1945	627,937	411,600	65.5	8.4	1.02
1946	511,389	337,871	66.0	10.9	1.03
1947	536,962	416,838	77.6	18.0	1.07
1948	569,947	470,784	82.6	13.6	1.18
1949	522,268	384,092	73.6	5.3	1.19

C. INEDIBLE TALLOW AND GREASE [1]

Year	Total Consumption	Consumption in Soap	% of Total Consumed in Soap
1936	930,506	758,734	81.5
1937	891,569	707,756	79.4
1938	946,808	798,623	84.4
1939	1,085,010	905,897	83.5
1940	1,241,198	1,043,342	83.8
1941	1,660.756	1,367,790	82.2
1942	1,859,765	1,527,897	82.1
1943	1,759,248	1,360,097	77.5
1944	1,922,714	1,529,749	79.6
1945	1,838,771	1,363,934	74.3
1946	1,676,607	1,209,839	72.0
1947	1,881,598	1,525,747	81.0
1948	1,781,942	1,451,454	81.4
1949	1,663,688	1,345,597	80.9

[1] Bureau of the Census Animal and Vegetable Fats and Oils 1936-40, 1940-44, 1942-46 and 1945-49.

[2] Prime tallow in carlots, Chicago, from Fats and Oils Situation No. 147, Feb. - March 1951, P. 21.

[3] Yellow grease, loose, Chicago, From Fats and Oils Situation No. 147 - P. 21.

The data in this table reveal the importance of soap as a market outlet for both grease and inedible tallow. For example, in 1936 when only 930 million pounds of inedible tallow and grease was factory consumed by industry, soap consumption accounted for over 758 million pounds, or 81.5% of the total. In 1949 when consumption of these two materials had increased to over 1663 million pounds, soap consumption still kept pace, with a usage of over 1345 million pounds or 80.9% of the total. This high diversion of inedible tallow and grease to soap use has remained fairly constant over the years with the exception of the war and immediate post war years as the tabulation under C of Table 1 indicates.

Inedible tallow has been displaced to a small extent by grease as a soap making fat, the usage having declined from approximately 90% to 80% while that of grease has risen from about 50% to 70%. The principle rise in grease usage took place during the war years when tallows were in short supply, and in the face of an adverse price structure (Column 6, Table 1 B), which at that time was fixed. The continued use of grease in high percentage in the post war years may be attributed to better processing, better methods of handling and to a more favorable price relationship to inedible tallow, exceeding even the pre-war ratio.

At present, however, the relation of inedible tallow and grease to one another is less important than their combined usage in soap, which in 1949 was 80.9% of their total consumption. Of the total consumption of inedible tallow and grease 169,378,000 pounds or 10.1% was converted to fatty acids, leaving

148,713,000 pounds or 8.9% for use in sulfonated oils, greases, textile cutting oils, etc. The greatest concern, therefore, is for the use of tallow in soap and the diversion of its uses from this product because of synthetic detergents. Tariff reports show that total production (100% active basis) of surface active agents including an almost constant 40 million pounds of sulfonated oils has more than tripled in the last six years.

PRODUCTION OF SYNTHETIC DETERGENTS (100% ACTIVE)

1945	-	184,442,000 lbs.
1946	-	242,174,000 lbs.
1947	-	291,161,000 lbs.
1948	-	374,715,000 lbs.
1949	-	429,890,000 lbs.
1950	-	676,346,200 lbs.

The estimate of bulk detergents for 1949 is placed at about 1.2 billion pounds of which about 900 million pounds were retail products almost exclusively within the class of granulated detergents.

The Census of Manufacturers report of soap production for 1947, with fat requirements (estimated) is as follows:

TABLE 2

(In Millions of lbs., - 1947)

	Type of Product	Amount	Fat Requirement
1	Toilet Soap	555	500
2	Granulated Soap	1522	1000
3	Laundry Bar Soap	791	382
4	Soap Chips	427	350
			2232
5	Washing Powder		
	Abrasive Cleaners	795	121
	Liquids and Paste		
	Mechanics and Medicated		
			2353

The estimated retail and industrial split of bulk synthetic detergents calculated on a 35% active basis is as follows:

TABLE 3*

BULK SYNTHETIC DETERGENT PRODUCTION IN MILLIONS OF POUNDS

	1939	'40	'41	'42	'43	'44	'45	'46	'47	'48	'49	1950
Retail	100	100	100	100	100	100	150	300	525	775	825	900
Industrial	70	80	80	80	100	140	150	150	175	200	250	300
Total -	170	180	180	180	200	240	300	450	700	975	1075	1200

* Data obtained from trade estimates.

This agrees with the American Soap Association reports fairly well, when it is considered that in 1948 only 17 companies were reporting production, and in 1950 the percent active ingredient in retail synthetics had fallen to about 22% due to the great climb of heavy duty products.

There is no indication that synthetics have reached a saturation point. Summarized data covering 9 widely separated cities (Omaha, St. Paul, Indianapolis, Milwaukee, Columbus, Sacramento, Fresno, Modesto and Rockford) and the questioning of 862,000 families gives weighted average figures as follows:

TABLE 4

	1947	1948	1949	1950
For washing fine fabrics Synthetic detergents used, % of total	28.6	31.2	34.5	37.2
For washing dishes Synthetic detergents used, % of total	36.4	44.2	54.0	56.8

The steady climb in these two important categories of use is taken to indicate an average increase of about 4% in retail products, equivalent to 50,000,000 pounds (since we can consider most of the increase due to retail sales.)

This represents an equivalent soap powder displacement which, on a 60% fat basis, means a displacement of 30 million pounds of soap fat per year. It is estimated that on a gross retail production of 900 million pounds, the equivalent of 540 million pounds of fats would be displaced representing at best 350 million pounds of tallow and grease (such products will run about 65% tallow and grease, the balance being foots and vegetable oils). Although the total fats and oils going to synthetics in 1950 was placed at 65 million pounds (Fats and Oils Situation October, 1950), it is estimated that not more than 10 million pounds would be used in retail detergents,

so that fat diverted to this use is negligible. A fallacy of thought is that this loss of tallow and grease business could be regained by causing synthetics to be fat-based. Taking the alkyl sulfate as an example, the tallow derivative contains 79% fat, and lauryl sodium sulfate, 74% fat. A 22% active detergent would therefore contain approximately 17% fat, so that 900 million pounds of such detergent could be made from 153 million pounds of fat, and the majority of this would be coconut oil. However, such a gain is not to be ignored and data given under Section 2, Substitution Products, Halogenation has something to say along this line. Actually, fat has not made much headway into retail detergents. Only one product appears on the present market; its estimated fat usage per year has been placed at 60 million pounds representing a production of about 350 million pounds or about 13 million cases. Up to 50% tallow or grease can be substituted for coconut oil in this formula and there is good reason to believe this is being done at the present time. This would mean an additional use for tallow or grease of up to about 25 - 30 million pounds.

The above discussion is designed to lay the ground work for an approach to profitable lines of research. It shows that the use of tallow, per se, is still very important, that detergents have made the situation alarming, and that a solution to the problem is not going to be found by converting such products to a fat base. The use of fat has been so well established that only major chemical modifications or deversions of other oils to new fields will be of interest. Such processes will be examined, particularly in reference to soap uses itself. In respect to the 10.1% (of total tallow and grease) diverted to fatty acids, the multiplicity of uses possible is most interesting and considerable space is given to their discussion. In 1949, 394,826,000 pounds of fatty acids were produced from vegetable, animal and fish oil sources, plus an estimated 200,000,000 pounds of fatty acid consumed in continuous soap processes which do not enter census figures. It is believed that the established use of soap is such that the diversion of 300-400 million pounds of tallow to new uses would very greatly stabilize the market. Doubling or tripling fatty acid production would be such a move. This is by no means beyond reason.

Present continuous fat splitting capacity is estimated from data gathered in this survey, at 400 million pounds; Twitchell fat splitting capacity is estimated at 300 million pounds for a total of 700 million pounds. This would be a minimum figure since soap plant capacity was not available and was therefore conservatively estimated at 200 million pounds.

To provide a background of data for proper evaluation of fatty acids and derivatives the following is presented:

TABLE 5

PRODUCTION OF FATTY ACIDS 1949 (POUNDS). CENSUS DATA

1. Fatty acids from coconut oil - - - - - - - - - - - - - - 37,642,000
2. Vegetable oil fatty acids from miscellaneous oils,
   such as linseed, castor, cottonseed, soybean - - - - - 17,174,000
3. Vegetable oil fatty acids from foots, principally
   cottonseed foots and soybean foots - - - - - - - - - - -134,561,000
4. Fatty acids from tallow - - - - - - - - - - - - - - - - -119,015,000
5. Fatty acids from grease - - - - - - - - - - - - - - - - 50,363,000
6. Fatty acids from hydrogenated animal fats- - - - - - - - 20,138,000
7. Fatty acids from miscellaneous primary fat sources,
   excluding vegetable but including marine oils - - - - - 4,538,000
8. Fatty acids from refuse fats, chiefly recovered
   palm oil from the tin plate industry- - - - - - - - - - 11,350,000

Sub Total - - - -394,826,000

To this must be added fatty acids split by continuous
processes and converted directly to soap and reported
as consumed in soap (approximate)   200,000,000

Grand Total (approximately) - - 600,000,000

Vegetable oil foots are used largely as a source of fatty acids. The
134,561,000 pounds in the table could be about doubled, if necessary, since
about 50% goes to the soap kettle in some form or another. On the other
hand, coconut, tallow and grease fatty acids are not derived to any great
extent from the foots but are largely derived from the fats themselves.
The foots are consumed in soap, with small exception. Tall oil is being
used to the full extent of its production which amounted to 250 million
pounds in 1949, 310 million pounds in 1950, and probably 330 million pounds
in 1951. Its recovery is fairly well established at the present time and
although there is a steady growth noted over the three years given, it is
felt that present production is approaching a peak limit. First, it is a
secondary product dependent on the production of pulp from the southern
pine. This yields about 60 pounds of tall oil per ton of pulpwood processed.

Not all producers are recovering their tall oil, but at the present rate of
pulpwood production, which averages 550,000 tons per month, the total tall
oil available would be not over 400 million pounds per year. Present re-
covery is thereofre over 80% of the available supply. Second, there is some
possibility of southern hardwoods being used to replace the pine. Develop-
ment along these lines will reduce tall oil production since such woods
have no recoverable rosin and fatty acids. Third, the extension of tall
oil recovery to pulping operations on northern pines has not been very
promising to date because of the low fat content of these woods. A few
mills in certain sections are finding recovery profitable, but it appears
very doubtful if this will develop into any large scale source of supply.

With these factors in mind, it is doubtful that tall oil production will increase by more than 25% over its present rate of production during the next ten years.

Considering, therefore, both vegetable oil foots and tall oil as additional sources of fatty acids, it must be concluded that any large increase in fatty acid production over present rates in excess of about 200 million pounds would have to come from tallow. The principal acids with which we are directly concerned are stearic, palmitic and oleic. To these must also be added the derived acids from the fission of oleic acid, namely, pelargonic and azelaic.

As a further help in discerning productive research, the following uses of animal fatty acids are given, based on the Census data, as modified by the interviews.

TABLE 6

Uses of Animal Fatty Acids

(A) STEARIC (49,363,000 pounds in 1949)

1.	Rubber, chiefly synthetic. (Single pressed stearic)	25.9 %
2.	Chemicals, including edible emulsifiers, ester plasticizers, etc.	13.3
3.	Cosmetics, shaving soaps, creams (Triple pressed stearic)	20.2
4.	Lubricating greases	6.4
5.	Polishes, floor waxes	6.4
6.	Candles	4.8
7.	Mould release powder (plastics, rubber)	3.6
8.	Metal working. Buffing compounds (single pressed)	2.1
9.	Waterproffing, cement. Metal salts.	1.9
10.	Ceramics	1.9
11.	Resins, as plasticizers and as chemical ingredient	1.8
12.	Textiles, in cationic softeners, waterproofing, etc.	1.6
13.	Pharmaceutical	1.6
14.	Protective coatings, such as rubber and cloth	1.7
15.	Paint and varnish, as flatting agent	1.0
16.	Wire drawing	1.0
17.	Crayons and chalk, phonograph records, as binder	0.9
18.	Matches, putty	.8
19.	Sulfonated acids, as emulsifier	.2
20.	Paper sizing	.2
21.	Insulation, linoleum, leather	.3
22.	Glue and adhesives	.1
23.	Chlorinated products, as plasticizers	.1
24.	Printing inks	.1
25.	Miscellaneous uses	2.4
		100.0 %

(B) OLEIC (46,168,000 pounds in 1949)

1. Soap. (Liquid soaps. This material is at present meeting stiff competition from tall oil, synthetic detergents and other vegetable oil fatty acids)   28.0 %

2. Chemicals, including ore flotation derivatives, synthetic detergents and other surface active agents   28.0

3. Textiles, including 2.1% of total as sulfonated product, balance as softeners   9.6

4. Cutting oils, metal treating   8.6
5. Lubricants and greases   3.9
6. Polishes (shoe, furniture)   3.8
7. Asphalt   3.0
8. Protective coatings   3.0
9. Rubber, as part of the formula   2.5
10. Putty, caulking compounds   2.9
11. Petroleum de-emulsifiers   1.7
12. Leather processing   2.6
13. Cosmetics and pharmaceuticals   0.4
14. Printing inks   .3
15. Hydraulic brake fluids   .2
16. Insulation   .1
17. Core oils   .1
18. Alkyd resins   .2
19. Miscellaneous   1.1

                                                     ─────────
                                                      100.0 %

(C) MIXED (22,030,000 pounds in 1949)

1. Lubricants and grease   34.8 %
2. Soap   21.7
3. Rubber   20.2
4. Chemicals   12.1
5. Paint and varnishes   4.2
6. Protective coatings   1.5
7. Plastics (as part of formula)   1.5
8. Leather   1.4
9. Metal work, mold lubricants, etc.   1.4
10. Textile and fiber softening, etc.   0.8
.. Miscellaneous   .4

                                                     ─────────
                                                      100.0 %

(D) HYDROGENATED (20,138,000 pounds in 1949)

These are manufactured to substitute for the higher priced stearic where the
higher content of true stearic acid is unimportant or is to be preferred.
Such substitutions occur chiefly to replace stearic acid in rubber and in
chemical derivatives.

1.	Chemicals	67.2%
2.	Paint and Varnish	8.8
3.	Lubricants and grease	7.7
4.	Rubber	5.7
5.	Soap	4.7
6.	Textile (Sulfonated products)	2.9
7.	Linoleum and oil cloth	0.7
8.	Metal processing, mold, wire drawing, etc.	.6
9.	Pharmaceuticals	.2
10.	Glues	.2
11.	Protective coatings, paper, plastics	.2
12.	Miscellaneous	1.1
		———
		100.0%

Two major conclusions from the interviews were:

    (1)   The adverse effect of the instability of the price of
            inedible tallow on research, and

    (2)   The lack of a coordinated group of persons to direct
            research on tallow, grease and lard.

Companies which deal exclusively with fats are not generally aware of the
significance of this fluctuation as a drawback to the use of their products.
Such companies would be the renderers and the fatty acid producers, primarily.
The companies having products which are both fat- and petroleum-derived are
sensitive to such fluctuation in price. For example, soapers who are now
making non-fat synthetics are very pleased with the price structure of their
new raw materials as compared with fats. It is quite possible that this may
actually influence their research and production.

Companies that deal primarily in petroleum or coal tar derivatives look upon
fat research with great reluctance. A process that looks good today will be
shelved tomorrow, and vice versa. As soon as money is invested in a plant the
company stands to lose terrifically with a slight change in price. The fur-
fural process for fractionating glycerides is an example. A plant designed
for up-grading soybean oil glycerides and dependent on a a 3-4¢ margin between
soybean oil and linseed oil, was forced to shut down when the margin be-
came 2¢, as in February, and 2-3/4¢, as of July 13, 1951.

No better example of price fluctuation in the fat field is available than
that noted during the course of this survey. In February, 1950 the price
for No. 1 tallow was around 12¢. Then for about 4 months it was at an
unprecedented low of about 5¢. In the fall it rose, until those inter-
viewed wanted to know why there was any need for a program on tallow as it
was in short supply at 15¢ or so. It finally rose to 19¢, a ceiling was

put on it at 15¢ and now after 18 months it is back to 8¢. In May, 1952, the price was 5¢ again.

The problem of the price fluctuation of tallow and grease is very complex and stems partly from its tie in with oils and fats, in general, and also to the fact that the market is dependent for pricing on the flow of only a small portion across its threshold. There is considerable material sold on contract (probably the majority) based on the market price as of day of delivery, or any other suitably designated day. This situation is extremely bad for any intensive research problem. No evidence was noted, however, of any attempt on the part of large users to make purchases other than in an orderly way to meet their week to week requirements.

We now come to the second major conclusion from the interviews, namely, the lack of a coordinated research program. This is essential to any program for finding expanded uses for inedible tallow and grease. The diverse interests must pass through a central clearing house and be balanced so that research work done on oleic and stearic acids will be approximately the same, and the uses for one will not markedly exceed those for the other. To expect individual companies to do this research and give it away is unreasonable. In the first place, any company doing research is doing it mainly for its own interests. If it is studying oleic acid, for example, it is not concerned whether it obtains it from tallow, vegetable oils or tall oil. Work that is done is fenced in with patents. As long as tallow had a steady and expanding market in soap and related products, there was little apparent need for research. This situation is no longer tenable.

The framework for organized research exists in the various renderers associations. For various reasons, mainly financial, little organized private work to date has been carried out on inedible animal fats. The renderers themselves, being small in general, have little facility for doing research and in this respect differ very much from the producers of other domestic oils such as cottonseed, linseed, soybean, etc.

The following suggestions represent a brief synopsis of opinions expressed during the interview by a wide range of interests:

(1) Direction of the research might conceivably be done by a committee selected from industry. The research proper could be handled in the laboratories of the producing and consuming companies or research institutes, and published through normal channels.

(2) The industry should establish a secretary and full time director to contact industry and act as nerve center for all activity.

(3) The group should be industry wide and should embrace producer and consumer as well.

(4) It should avoid patents on work done or should keep such arrangements to a minimum.

(5) It should correlate and suggest the direction of work only.

(6) It should reduce duplication of work by making known periodically, work being done under its direction or suggestion, and by having new work checked and published by selected companies.

A study of existing groups and their method of working would be beneficial. Suggested organizations include the ASTM Committee 12 on methods of analysis, the Tall Oil Association, The American Soap and Glycerine Producers Association, The Tin Committee at the Battelle Memorial Institute, the A.P.I. committee on petroleum hydrocarbons, the American Meat Institute at Chicago and The National Printing Ink Research Institute, Bethlehem, Pennsylvania.

The feelings of the industry on this subject were briefly as follows:

<u>LARGE FAT AND FATTY ACID PRODUCERS</u> - Money spent in their own laboratories pays greater dividends than money spent outside. In general they were not interested.

<u>RENDERERS</u> - They are not equipped, generally, for research. Their chief difficulty in organizing a central research group is fees. No one wants his neighbor to know how much business he is doing. This can be avoided by having an independent accounting firm examine the books of each company and assess a fee, proportionate to its financial status, to meet the required budget. The amount so specified would be kept confidential between the accounting firm and the individual company.

<u>THE INSTITUTES</u> - They are ready at any time for research fellowships.

<u>THE UNIVERSITIES</u> - They are ready to carry on any research problem within their scope of interest. Usually this scope is limited to fundamental research.

<u>LARGE USERS OF FATS</u> - Like the packer, the general attitude is that their own research organization is sufficient.

The obstacles for positive action are considerable and a protracted period of 5¢ tallow would probably be required as an incentive to constructive thinking on this subject.

Research on Inedible Animal Fats

1. RENDERING

The methods of rendering have been well standardized. The quality of the product of dry rendering practiced by the renderers, in general, is subject to abuse by the operators through faulty control. Procter and Gamble have issued a small booklet on the subject called "Better Rendering" designed as a text for this operation. Lever Brothers (U.S. Patent 2,455,374) mention hydrated silica (0.1 - 5%) as an aid to improving the color of the rendered product. Solvent rendering is being used extensively in the midwest and to some small extent in the east to reduce the fat in cracklings from 7% to about 3%.

2. PROCESSING METHODS TO PURIFY FATS

(A) Bleaching

Bleaching processes are generally adsorption ones using activated clays. No startling development has been noted but over the years the quality of bleaching clays has steadily improved. The decolorization of tallow by the Solexol system (U.S. Patents 2,454,638 and 2,467,906) is satisfactory, but in order to make it commercially useful there should be spread of 2¢ per pound between Fancy and No. 1 grade. This allows about 1-1/2¢ per pound for operating and overhead costs plus 1/2¢ allowance for a small foots loss. On a 5¢ tallow this foots loss would shrink considerably, so that the operating margin between Fancy and No. 1 grade tallow on such basis would approach 1-1/2¢. Unfortunately, the margin between grades shrinks with low prices, so that the Solexol process offers the least help to the renderer at a time when he most requires it.

The Furfural Process (U.S. Patent 2,200,390-1, 2,278,309, 2,291,461, 2,313,636, 2,316,512, 2,390,528 and 2,423,232) modified to include naphthol, is claimed to be useful as an oil decolorizer. It has not been used on tallow as far as we are aware.

Chemical bleaching is done in a small way. The sodium chlorite and chlorine dioxide method (U.S. Patents 2,431,842 and 2,430,675) has caused quite a stir in the commercial field through its use by render ers. It is claimed that soap made from such bleached fats revert.

Successful use of the chemical bleaching process in renderers' plants for over a number of years has been claimed. The process is adaptable to pipeline bleaching by a continuous method and soap does not revert unless the tallow is overbleached. Chlorosubstitution products are formed by the prolonged contact between fat and chlorine. Under such circumstances there is good reason to believe that reversion can occur, although insufficient work has been done to put the point beyond dispute. This process as a method for tallow and tallow fatty acids should be investigated more fully.

Hydrogen peroxide has been used as a bleach for fatty acids. (Brit. Patents 577,879-880). The claim is made that the soap stock does not revert.

Chemical bleaching, except on specialty compounds, is not favored by the soap industry.

(B) Alkali Refining

This is relatively unimportant to tallow and grease. Losses are low since well rendered tallow contains little mucilaginous matter. Since the foots are also used as soap stock, there is small incentive to keep losses down by such methods as centrifuging, etc.

(C) Deodorizing

The steam distillation method has been greatly improved in the past 20 years by use of tighter equipment, higher vacuums, de-aerated and superheated water, and drop tanks for cooling before filtering. The most recent methods are continuous and semi-continuous. The application of deodorization to lard is as easy and as satisfactory as with any other fat.

3. PROCESSING METHODS TO SEPARATE THE GLYCERIDES

(A) Solvent Extraction (Solexol Process)

This process is the same as that mentioned above under decolor-ization. The fat and propane are passed countercurrently to one another through a column of large diameter at a definite temperature, pressure and ratio of solvent to fat. The color-ing matter, saturated glycerides, unsaturated glycerides, and vitamins (if present) have different solvent properties so that a variety of products may be obtained merely by changing the conditions of temperature, pressure, solvent ratio and throughput of the column. It is possible, for example, to separate tallow into a bleached fraction and a colored fraction. The color bodies are removed as a bottom fraction from the column. Under other conditions of operation it is possible to include in the bottom fraction color bodies plus highly unsat-urated glycerides. The top fraction may be made to contain the more saturated glycerides and the vitamins. By using several columns it is possible to separate all four fractions. Menhaden oil of iodine value 180 has been separated into fractions of iodine value 155 and 205 with one pass, at 1-1/4 to 1-1/2¢ per pound, including royalty charges. No color bodies were removed, hence no foots loss was present, as in the case of decolorizing tallow, to raise the cost figure.

At present, the process has little to warrant its use for tallow processing for two reasons. First, the separation of the indi-vidual glycerides is not as clear cut as that obtained on the fatty acids, and secondly, a modified propane crystallization process, about to be described, can apparently accomplish the same separation at a lower cost.

(B) Solvent Crystallization

This process is also known as the Destearinizing Process; pro-pane is used as in the Solexol Process. In solvent crystalliza-tion, the oil-propane mixture is batch chilled to -25° C. or lower, held at that temperature for a short period to promote crystal formation and then vacuum filtered at a low temperature. One unit operating on fish oils separates glycerides with an iodine number of 180 into two fractions having iodine numbers of 155 and 205, respectively. It is thus seen that the Solexol

and Destearinization processes accomplish the same separation on Menhaden oil, although the Solexol process, by its ability to decolorize and remove vitamins as well, is apparently more versatile. Plant cost for solvent crystallization is believed to be $600,000 for a 50-ton per day plant. Total operating cost is placed at 0.50¢ per pound which is less than that for the Solexol operation. In respect to tallow grease and lard, this type of operation and plant has a large potential use as a means of preparing lard oil, grease oil, oleo oil and oleo stearin. The process has much to recommend it from a cost point of view.

(C) Pressing

Although this method is still used mainly for the manufacture of lard oil from lard, it is probably obsolete now, in view of the solvent separation methods.

4. PROCESSING METHODS TO MODIFY A FAT CHEMICALLY

(A) Interesterification

This process is relatively unimportant as far as tallow, grease and lard are concerned. There are numerous patents in this field.

(B) Double Bond Isomerization

Oleic acid can be converted to palmitic acid by alkali fusion, and at one time such a process was in operation commercially in France. Elaidinization is unsatisfactory as it is not a complete reaction, stopping at the 2/3rd mark. The best catalyst, selenium, is also poisonous; sulfur and oxides of nitrogen are also employed. Conjugation and polymerization is, generally speaking, not a part of animal fat chemistry, but such processes have been used to eliminate the polyunsaturates from a tallow in order to increase the purity of the derived oleic acid.

(C) Double Bond Addition

Hydrogenation is the most important and is, of course, well known. (1) Selective hydrogenation of tallow as a means of preparing pure oleic is useful. (2) Lard has a variable unsaturation which requires a touch of hydrogen to make it uniform. It has been stated that the presence of some linoleic in lard is of great benefit from a nutrition point of view. If a method were available to hydrogenate lard uniformly at small expense to an iodine value just low enough to insure the absence of linoleic acid, then the arguments in favor of leaving such highly unsaturates in the lard would be weak compared to the advantages to be gained in stability by taking them out.

There is a need under both 1 and 2 above for a continuous process of hydrogenation, using a fixed catalyst and controlled by automatic means. A new source of hydrogen, from thermal decomposition of NH_3, is available to fat processors. This is being widely used where the volume of gas required does not warrant a full scale propane or other type of plant with its accompanying large capital outlay.

SECTION 2

FATTY ACIDS AND DERIVATIVES

1. PROCESSING METHODS TO OBTAIN FATTY ACIDS

The Twitchell process for fat splitting is now considered obsolete. Present fatty acid production is approximately 400 million pounds per year by continuous splitting of fats and 200 million pounds per year by Twitchell splitting. The patents for continuous hydrolysis are numerous. Alcoholysis of glycerides to simple esters is worthy of study in view of the possibilities of making the process continuous.

A recent patent for splitting tallow uses Skellysolve K and concentrated sodium hydroxide at 400° F. for 7 min. at 100 psi.

Distillation, either continuous or batch, is the most common way of purifying fatty acids. All modern plants of any size are generally continuous. Where separation of fatty acids is desired, the still is equipped with a fractionating column also, generally of about 30 theoretical plates, and is capable of separating oleic and stearic acids from palmitic acid to the extent of 90% or better. No development in fat chemistry has progressed further in the past twenty years than this phase of processing. The most modern stills use very little steam to assist volatilization of the acids but an extremely high vacuum. One of the better types of stills employs a separate stripping tower using steam plus a fractionation column where the vacuum is as low as 2 mm. or less. In a non-fractionating, continuous flash-film still, designed for continuous soap making operation, pressures as low as 0.2 - 0.3 mm. and no steam are employed.

The cost of distillation is quite low as far as plant operation is concerned. For example, continuous distillation of tallow fatty acids are estimated on a 2-1/2 ton per hour plant as follows:

	Cost in $ per 1000 lbs.
Labor	0.40
Services, steam power, water, etc.	0.13
Overhead	0.40
Repair and Maintenance	0.10
Amortization of plant over 10 yr.	0.50
	$ 1.53 (0.15 cents per lb.)

To this must be added the loss due to polymerization, oil residues, etc.

Still design will continue to improve and become more uniform. Probably the next step in fatty acid separation will come through the increased use of distilling the esters when it becomes more feasible to produce them through alcoholysis, etc. Only one firm is believed to be doing so to date. The advantages of such a procedure over straight fatty acid distillation are greater stability of product during intermediate stages of manufacture and lower capital cost of equipment through the use of less expensive acid-resisting alloys.

Separation of the fatty acids by pressing is now obsolete. The method is being rapidly replaced as equipment wears out. Solvent crystallization methods developed through petroleum de-waxing techniques are fast becoming important. There are two chief methods which differ substantially only in the solvent used, namely, aqueous methanol and acetone. The secret of good crystal formation is to have the acids present in reasonable agreement to their natural eutectics and to have a slight amount of neutral fat present (0.2 - 3-1/2%). The crystals in both solvent methods are filtered through a continuous vacuum or pressure type of filter and are washed on the press screen with fresh solvent. At present, oleic is not separated from linoleic acid by low temperature crystallization on a commercial scale.

The propane destearinization process has been mentioned as a possible process for use on fatty acid separation. Considerable research data have been accumulated on this from laboratory experiments and the method has been used on an experimental basis. Liquid extration processes such as the furfural process and Solexol process have not apparently been used for this purpose to date, although the furfural process has been mentioned as a method for separating fatty acids.

A new method of separation, not applied as yet commercially, is chromatographic separation. This process has long proven very useful as a laboratory tool. It may be applicable industrially with proper automatic control. A plant of this kind is in operation for the removal of benzene from petroleum oils.

Another method, using a ketone, crystallizes stearic acid up to a purity of 99% without refrigeration. Of interest also is the method of separating fatty acids by the formation of urea complexes. Research is required to determine whether these methods will be useful in the commercial separation of tallow fatty acids. Laboratory separations are efficient especially when combined with crystallization methods.

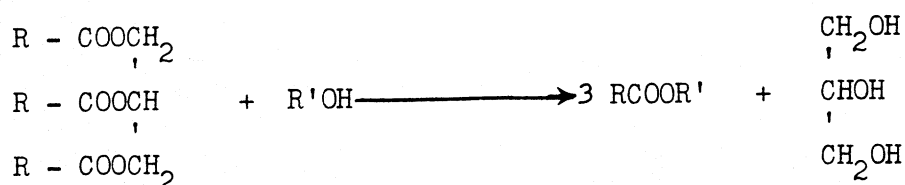2. PROCESSING METHODS TO CHEMICALLY MODIFY FATTY ACIDS

   (A) Carboxyl Modification

ESTERS

The general method of preparation consists of direct esterification of the fatty acids in the liquid phase in an ester kettle. The water formed is removed by use of air, an inert gas, vacuum, azeotropic distillation, or combinations of these methods. There is no single method applicable to all types of esters since these vary

widely in their solubility, boiling points, stability and other characteristics. Catalysts may be necessary, such as H_3PO_4, H_2SO_4, $ZnCl_2$, aryl sulfonic acids, caustic soda, sodium methylate, etc. In special cases it is necessary to use other derivatives for the esterification such as the acid chloride, acid anhydride, etc.

Another method of ester formation is alcoholysis of glycerides with or without pressure.

$$R - COOCH_2$$
$$R - COOCH \quad + \quad R'OH \longrightarrow 3\ RCOOR' \quad + \quad \begin{array}{l} CH_2OH \\ CHOH \\ CH_2OH \end{array}$$
$$R - COOCH_2$$

This important process has been dealt with previously as a means of preparing fatty acids. Fatty acids from castor oil are commonly prepared this way. Interesterification consists in the exchange of alkyl radicals between two esters, also known as ester interchange, and between an ester and an acid, known as acidolysis.

$$RCOOR' \quad + \quad R''COOR''' \longrightarrow RCOOR''' \quad + \quad R''COOR'$$
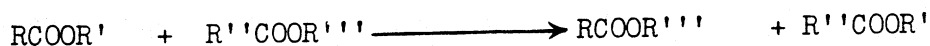
The more volatile ester is driven off to drive the reaction to completion.

$$RCOOR' \quad + \quad R''COOH \longrightarrow R''COOR' \quad + \quad RCOOH$$
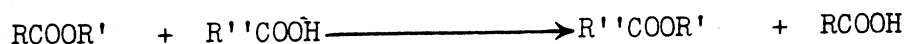
In this last case the more volatile acid is distilled off. As a practical example, palm oil containing a high percentage of free acids, is treated with coconut oil. The free palm oil acids are esterified and the liberated lower boiling coconut acids are removed.

The esters differ from the amides and amines in their instability toward acid and alkali and for this reason are most suited to processes and products where they are used under neutral conditions or where they are transitory materials, as in foods, etc.

To deal with the multiplicity of products available and in present commercial use, it is best to consider the properties of an ester as that of its two constitutents, the acid and the alcohol. With such fatty esters as methyl stearate, ethyl palmitate, etc., the properties of the fatty acid far outweigh those of the short chain alcohol. With hexitol monopalmitate, polypropylene, glycol monostearate, etc. the properties of the alcohol may largely mask those of the acid. With ethylene oxide addition to the fatty acid, all grades of intermediate properties are available depending on x in the following structure:

$$RCOO\ (CH_2CH_2O)_x CH_2CH_2OH$$
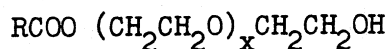
The most important class of esters are the triglycerides, previously dealt with under fats and oils. The next most important class from a commercial production point of view are those from polyhydric alcohols, such as glycerine, the glycols, mannitol, hexitol, sucrose, pentaerythritol, etc. These products are widely used as emulsifiers, in foods and pharmaceuticals. Probable production of such types is estimated to consume 22 million pounds of animal fats per year of which probably 10 million pounds are monoglycerides of stearic acid for edible, cosmetic and pharmaceutical purposes. This estimate is based on scattered data from producers interviewed, plus Census reports.

The simple esters, such as the methyl and ethyl esters of oleic and stearic acids and azelaic and pelargonic acid plus miscellaneous others not included above, consume about 3 million pounds of animal fat. This estimate does not include such derivatives as sebacic acid esters widely used as plasticizers, since these acids are largely made from imported castor oil.

Oxidation costs of producing azelaic acid largely determine the extent to which sebacic acid could be replaced, it is believed, although definite information as to the relative merit of this product in comparison with sebacic acid derived products was not forthcoming from the interviews, largely, no doubt, because the producers of azelaic and pelargonic derivatives themselves did not have the data.

As mentioned above, the properties of the esters are determined largely by the constituent acid and alcohol. For example, the methyl ester of oleic will be modified by whatever additions may be made at the double bond. Methyl 9,10-epoxystearate is such a product. (Evans et al., U.S. Pat. 2,237,729 (1941)). Alpha-hydroxy stearic acid, and pentachloro- and dichlorostearic acid are reported to be useful as plasticizers and lubricant additives. Lubricant additive uses are reported to consume about 200,000 pounds of triple pressed stearic acid a year. Usually the ester of the unsaturated acid is more stable than the free acid itself. Castor and tung oil esters of pentaerythritol and dipentaerythritol are very fast drying. This last example is by way of illustration only since we are primarily concerned here with tallow, grease and lard, and their derivatives. However, in any evaluation of esters the type of products obtained by double bond modification, addition or substitution must be considered as yielding a new product. The possibility of polymerization or other reaction between double bonds of two oleic molecules is another type of modification which would yield interesting diesters. Esterified sulfonated oils are being used as emulsifiers in cutting oils.

The esters find a wide use in a variety of ways in addition to those already mentioned. A few typical examples bearing on tallow-derived fatty acid esters follow:

   (1) Triethanolamine stearate, for laying dust in mines, roads, etc.

   (2) Partial esters of fatty acids with polyhydric alcohols useful for

(a) Preventing crystallization of stearin from salad oils

(b) As an ingredient of an all synthetic bar soap

(c) As a crumb softener for bread.

(3) Fatty acid monoglycerides as a defoaming agent for paper stock.

(4) Sulfonated butyl oleate

(a) As a textile softening agent.

(b) With metal salts, as an ingredient to waterproof cement.

(c) To petrolatum as a pharmaceutical base.

(5) Short chain esters,

(a) Dioctyladipate, as yarn plasticizers

(6) Esters from fatty acids and fatty alcohols, where one contains an hydroxy group, are useful as wax substitutes.

(7) As additives to greases and oils

(a) Glycerol monosterate

(b) Oleates

(c) Chlorosubstituted esters

(d) Polymerized esters

AN EXAMINATION OF THE ABOVE USES INDICATES, IN A BROAD WAY, THE MAIN TYPES OF OUTLETS FOR THESE PRODUCTS. THE LARGEST AT PRESENT IS IN THE MONOGLY-CERIDE FIELD. AS IT IS A WIDESPREAD CUSTOM TO PUT EMULSIFIERS IN SHORTEN-INGS, VERY LIKELY 40 TO 50 MILLION POUNDS PER YEAR OF MONOGLYCERIDES ARE BEING USED FOR THAT PURPOSE. EXCEPT AS ESTIMATED ABOVE IN THIS SECTION, THESE ARE MADE IN SITU AND THEREFORE FROM VEGETABLE OILS OR LARD. THE NEXT MOST INTERESTING USE IS 2c ABOVE.

ESTERS ARE NOT INTERESTING AS RETAIL DETERGENT PRODUCTS BECAUSE OF (1) A CHANGE IN BUYING HABITS WHICH IS TOWARD THE USE OF BUILT DETERGENTS (SUCH PRODUCTS CANNOT USE ESTERS BECAUSE THEY ARE UNSTABLE TO ALKALINE SALTS) AND (2) TECHNICAL DIFFICULTIES IN SPRAY DRYING WHICH GIVES A HIGH LOSS. IT IS DOUBTFUL IF SULFONATED MONOGLYCERIDES WILL EVER AGAIN BECOME AN IMPORTANT RETAIL PRODUCT.

ESTERS, SUCH AS THE POLYOXYETHYLENE DERIVATIVES, ARE SUGGESTED FOR RESEARCH AS ADDITIVES TO SOAP AND AS LOW FOAM NONIONIC DETERGENTS, PARTICULARLY SUB-STITUTED STEARIC ACID DERIVATIVES.

ESTERS ALSO FORM THE BASE FOR AN INTERESTING STUDY ON PROCESSING. THEY ARE MORE STABLE THAN THE CORRESPONDING ACIDS AND ARE MORE EASILY DISTILLED. RESEARCH ON THE POSSIBLE COMBINATION OF CONTINUOUS ESTERIFICATION WITH MODERN METHODS OF SOLVENT CRYSTALLIZATION OR EXTRACTION MAY PROVE VALUABLE, FROM AN EQUIPMENT AND PATENT ANGLE.

SALTS

The salts of the fatty acids may be roughly divided into two classes (1) the sodium and potassium salts, or hard soaps and soft soaps, respectively, and (2) the heavy metal soaps. The great majority of inedible tallow and grease finds it way to (1). A very much smaller portion, estimated at somewhat less than 100 million pounds finds its way to (2). The interviews with petroleum companies in general were negative in regard to specific types of use to which tallow is put, but practically all companies buy it or its derivatives in car lots to convert principally into such soaps as aluminum stearate, sodium stearate, calcium oleate, etc., as an ingredient of lubricating greases. A very considerable portion of lubricating greases is built with water soluble soaps indicating the overlap of functions among the salts.

Considering first the water soluble sodium and potassium salts, which represent by far the largest single outlet for inedible tallow and greases it is estimated from market data relating to soaps and synthetic detergents, that synthetics have displaced some 350 million pounds of tallow which would have normally gone to that market had synthetics been absent. Furthermore, at the present rate of growth of synthetics, another 30 million pounds of the fat market is being lost per year, of which about 25 million pounds represents tallow. This displacement will approach a limit since the synthetics are mainly in competition with soap powders whose total production in 1947 (Census of Mfg.) was 1,522,795,000 pounds. In that year year it is estimated that 525,000,000 pounds of synthetic detergents were sold (all in granular form) making a total consumption of such types of cleaners of just over 2.0 billion pounds. Since that time, overall soap sales have remained fairly constant while synthetics have advanced materially for the same period.

All companies making synthetics are not members of the Association of American Soap and Glyceride Producers and those not members generally produce for industrial consumption. The most recent estimate of total synthetics produced in 1950 is 1.2 billion pounds which allows approximately 900 million as retail package products, thus placing retail consumption of powdered detergents at about 2.4 billion pounds. How far synthetics will displace soap is very highly speculative but some consider that it can reach 2.0 billion pounds which would mean an overall displacement of about 550 million pounds of fat. These estimates for the most part are based on present commercial applications and uses. There is the category of toilet bar soaps which could develop a considerable market for synthetics to the displacement of soap, either by the successful formulation of either an all synthetic bar or a mixed soap plus synthetic bar. The 1947 Census of Manufacturers report placed the toilet soap category at 555,451,000 pounds, which is a considerable potential.

In investigating research work that is or should be done to increase domestic fat consumption, this present large outlet must be given first consideration because of the tonnages involved.

   (1) What research will expand present soap markets?

   (2) What research will expand the use of domestic fats in synthetics?

   (3) Who would be interested in carrying out product application research?

Item 1 - Research to Expand Present Soap Markets

Soap is so old that the pattern of its applications has been well established. As long as soap competitors, such as the sulfonated oils, etc., were of minor importance there was relatively little need for development work. With synthetics now occupying a large part of the detergent business, both retail and industrial.and with many companies doing planned market research, there is greater need than ever before for market and laboratory research on soap, to present scientific and unbiased reports to industry and to follow up new product and process development. The following illustrate this.

   (1) The use of 5% guanidine stearate in soap flakes is reported to improve its solubility and detergency on soiled dishes.

   (2) The use of an alkylphenoxy carboxylic acid salt, such as sodium p-octyl phenoxy acetate is claimed to increase the solubility and detergency of stearate and hardened whale oil soaps.

   (3) The addition of 2% of salts of ethylene diaminetetracetic acid to soap flakes greatly improves hard water stability. The effect falls off rapidly with an increase in temperature. The present use of such sequestering agents in bars is limited because it leaches out. Such types of sequestering agents are rather widely made and patented. If used in large amounts they could be used to prevent the precipitation of lime soaps when soap is the detergent. However, soap itself is able to sequester its own lime soaps if used in excess. Such addition, therefore, would have no great value unless the sequestering agent could be added to the water prior to its use in the rinse. This appears to be a rather impractical solution at the moment. However, the sequestering agents, as a material for addition to soap, should not be taken lightly and research on these materials should be given careful attention.

   (4) The use of amides in soap has been reported occasionally and requires further study.

The size of the market aimed at here is approximately 400-500 million pounds of tallow per year displaced from soap by synthetics. Whatever fraction of this could be recovered would depend on how thorough a job was done, how well the idea was explained, and to what extent existing patents could be cross licensed.

Item 2 - Research to Expand the Present Use of Fats in Synthetic Detergents

Individual developments are treated elsewhere but the relationship of their importance to domestic fat usage is here brought out. It can be shown for example that a fat converted to a synthetic detergent goes about 3.5 times as far as the same fat converted to soap. For this reason, even if all present production of retail synthetic detergents, estimated at 900 million pounds, were fat based, not over 150 million pounds of fat would be required for their production of which not more than 75 million pounds would be tallow and the balance coconut oil. Actually a leading synthetic detergent is fat based, and could very well account for a use of 25 - 30 million pounds of tallow. The present size of this retail market for fat therefore would be not more than 60 million pounds with a possible increase to 100 million pounds if expansion in synthetics continues up to 2 billion pounds. The discussion above is made to establish the size of the market.

Item 3 - Who Would be Interested in Carrying Out such Research?

(Promotion of Soap Usage as Detergents)

Soap producers are at present doing much development work. However, the large producers of soaps are also making synthetics and therefore have lost, to some degree, the point of view they had 10 to 15 years ago. The promotion of synthetics or soaps will vary to some extent with the price relationship of the raw materials. Since synthetics are built on a more stable price structure than are fats, the former are bound to be favored in development work.

The small soap companies generally do not have the facilities to do research work. The renderer, although vitally interested in the soap picture since he sells the vast majority of his product to the soap makers, has no individual or coordinated program on this subject. The packer, usually a soap maker also, is probably bearing the brunt of this work. It is the opinion here, based on the interviews, that a metamorphosis is taking place in the detergent industry - that tallow as a raw material for soap has lost a large portion of its market and that these facts should be recognized and a coordinated effort made to maintain and extend present uses by a program of market research and development.

The variety of heavy metal salts of fatty acids is large. For practical industrial application they may be classified briefly by their principal salts and use as follows:

1. The paint driers - The cobalt, lead and manganese salts of unsaturated acids, such as the linolenates and naphthenates, are catalysts for use as paint driers. This class has no interest in this investigation; it is an outlet for vegetable oils, mainly.

2. As catalysts for high temperature reactions, such as the oxidation of petroleum hydrocarbons, hydrogenations of organic compounds, as rubber accelerators, such as Pb oleate, in the manufacture of monoglycerides and in the reduction of fatty acids by hydrogen (Pb, Cd or Cu salts).

3. As dispersing agents, wetters and detergents, to suspend pigments in paints, sludge in lubricating oil, as dry cleaning soaps, etc. These are chiefly the salts of naphthenic acid and their formaldehyde condensation products.

4. For lubricating grease manufacture. These are generally the stearates, palmitates, oleates or tallow fatty acid derivatives of Na, Al, Ca, Mg, Li and Pb. The mineral oil is considered the lubricating material and the fatty acid soap is the bodying agent which keeps the lubricant in a solid form for easy application, such as in cup greases. The soaps are used for their properties of gelling and thickening. There is evidence also that the neutral soaps can actually be lubricants in themselves by the adhesion of the metallic ion to the metal surface of the bearing. The type of mineral oil used, additives added to the oil, temperature and condition of use all influence the choice of fatty acid and metal. The sodium and lithium stearates are used at temperatures above 100° C. Ca salts waterproof the lubricant. The petroleum companies, in general, make their own soaps and buy the necessary fats and fatty acids in tank car lots. Certain types of salts require special manufacturing technique and equipment, and many companies specialize in supplying the metallic soaps to the trade in various grades. The titer of the fatty acid used is important, so that normal stearic acid containing 45% stearic and 55% palmitic acid would give one type of grease, while hydrogenated tallow fatty acids containing 70% stearic and 30% palmitic would give another type. However, the variable of concentration, choice of metal ion, etc., give the manufacturer a choice of conditions so that the availability of fatty acids in a pure state from newer methods of processing (solvent crystallization, fractional distillation, etc.) is not expected to have much influence on grease manufacturing.

5. The metal soaps also act as thickening and stiffening agents for other materials than lubricants, such as paints. Al stearate is most commonly used, followed by Al oleate. Other uses are the thickening of gasoline for use in warfare (Napalm), and in the preparation of solid fuels. Co stearate is used in candles and asphalt as a hardener.

6. As a direct lubricant in

   (a) Wire drawing. The Zn, Na and Al stearates or the corresponding salts of tallow fatty acids are used. As simple as it may sound, the type of formula used in wire drawing is quite variable and depends on the type of wire being drawn, such as bronze, copper, steel, iron, etc.; plus the speed of drawing, size of wire and type of die. For small sizes, the lubricant is usually a solution of common sodium soap. The estimated yearly usage of wire drawing compounds is about 18 million pounds.

(b) Surface lubricants for molds and machine parts. The stearates of Ca, Zn, Pb are the principal ones.

(c) Internal lubricants, in tablets, crayons and pencils (Zn stearate), and in modeling wax, plastics, rubber, etc. (Pb oleate).

(d) Extreme pressure (E.P.) lubricants (Pb stearate or oleate.)

7. As a paint flattener, principally the stearates of Zn, Mg and Ca.

8. As waterproofing agents. The stearates of Al, Ca and Zn and Pb oleate are often used, especially where whiteness is a factor. Such uses include coatings on paper, textiles, wood and even on the surface of certain chemicals to make them free flowing. Application is made from a solvent. Zn stearate is of particular interest in textile work.

9. As fungicides and pesticides. The action depends on the hydrolysis of the metal salt and the poisoning effect of the soluble metal salt formed. Hg, Cu and Zn oleate (in order of decreasing toxicity) are used as fungicidal sprays, in marine paints, and in salves and ointments. Phenyl mercuric stearate, for example, is used to prevent mold growth in the fat liquoring of leather.

10. Cosmetics and Pharmaceuticals. Zn stearate which may be very finely ground, has mild antiseptic power.

11. Chemicals. Pyrolysis of the Ca salts gives dialkyl ketones and hydrocarbons. This reaction has long been known but to date has had little commercial application. A more important use of the heavy metal salts is in alcohol formation. Recent work shows that high yields of alcohols are possible by heating the lead, copper or cadmium salts of the fatty acids at temperatures approaching 400° under pressures of hydrogen up to 4000 psi.

12. Miscellaneous. In mordant dyeing, as an additive to lubricating oil (Cr, Ni, Pb oleates, etc.), and to improve the high temperature resistance of Al stearate greases by the addition of a small amount of Li stearate.

Al stearate in concentrations of 0.1 - 0.5% is added to lubricating oils as a pour point depressant.

Cr oleate in concentrations of 0.25 - 1.0% is added as an antifoaming agent in cutting oils. Ca stearate is used as an additive to diesel fuels.

THE MOST INTERESTING INVESTIGATIONS IN THIS FIELD APPEAR TO BE (1) THE USE OF THE METAL SALTS AS THICKENING AGENTS FOR THE PREPARATION OF SOLID FUELS AND (2) THE USE OF ADDITIVES TO PETROLEUM OILS IN SMALL AMOUNTS TO INCREASE LUBRICATION. CHLORODERIVATIVES OF FATTY ACIDS, FATTY ACIDS THEMSELVES, AND SODIUM ALKYL NAPHTHENATES ARE NOW USED EXTENSIVELY. THE LARGE TONNAGES OF LUBRICANTS INVOLVED MAKE THIS AN ATTRACTIVE FIELD EVEN WHERE ONLY 0.1% - 0.5% ADDITIVE IS INVOLVED. THE MAHOGANY SOAPS, LARGELY IN SURPLUS A FEW YEARS AGO, ARE NOW IN

GREAT DEMAND, WITH STOCK ALMOST NON-EXISTANT. THE USE OF SMALL AMOUNTS OF PROOXIDANTS FOR USE IN TOP LUBRICATION WOULD APPEAR ATTRACTIVE. THESE REDUCE CARBON FORMATION IN CYLINDER HEADS. AT PRESENT, RESEARCH LEANS TO-WARD THE USE OF NAPHTENATES. THE STRONGEST COMPETITORS IN THE FIELD OF METAL SOAPS ARE THE METAL SALTS OF PETROLEUM FATTY ACIDS AND OF THE NAPHTHE-NATES, THE LATTER HAVING SUPERIOR SOLVENT SOLUBILITY. IT IS QUITE UNDER-STANDABLE WHY THE PETROLEUM INTEREST WOULD FAVOR STABLE PRICED MATERIALS OBTAINABLE WITHIN THEIR OWN ORGANIZATIONS. THE ADVANTAGE FATTY ACIDS AND FATS HAVE IS THE CONSTANT COMPOSITION OF EACH PRODUCT SUCH AS SPECIFIC CHAIN LENGTH, KNOWN DOUBLE BOND POSITION, NON-BRANCHED-CHAIN ISOMERS, ETC. EVEN SO, THIS MARKET COULD BE LOST THROUGH INADEQUATE RESEARCH PROMOTING THE FAT INTERESTS, OR UNUSUAL AND VARIABLE PRICING CONDITIONS.

Salts of fatty acids with organic bases are one of the most important indus-trial outlets for fatty acids, particularly oleic acid. It is estimated elsewhere that in 1940 about 22 million pounds of oleic acid went into chem-icals, and a good portion of this, probably up to 10 million pounds, was first converted to an amine salt and further reacted to a substituted amide. Thus a large part of this production is formed as an intermediate.

Such products and the possibilities of such products have been, therefore, part of the discussion on Amides. A wide variety of detergent, emulsifying and wetting agents are prepared, however, simply by neutralizing the acid with an organic amino derivative such as monoethanolamine, hydroxyethylethlene diamine, guanidine, etc., without dehydration. The morpholine soap of oleic is used as the emulsifier in water resisting floor waxes and is prepared in situ.

Ethanolamine soaps are sold chiefly as liquid hand soaps. For this type of use, little expansion can be foreseen other than the occurring in the normal business cycle. Use of such products, however, in synthetic detergents and in regular soaps has been mentioned in the patent literature. The incorpo-ration of 5-10% in bar soaps to aid texture has been suggested. The use of 5% guanidine stearate in soap flakes to improve their solubility, detergency and stability to hard water has also been reported. Other fat and non-fat derived materials have been mentioned from time to time for purposes of im-proving soap products. These uses are not to be considered new outlets for fat, however, and may actually curtail them, since they replace soap in part.

THE CONCLUSION REACHED IS THAT THESE PRODUCTS OFFER LITTLE PRESENT INTEREST IN RESEARCH WITH REGARD TO INCREASED TALLOW CONSUMPTION.

AMIDES

The primary amides of the fatty acids are obtained commercially by passing ammonia through the fatty acids at high temperatures, resulting in dehydra-tion of the ammonium salt formed. This field is expanding. Although a large number of types of products are available, the amide is dependent for tonnage figures, in the main, on a comparatively few products. In checking over the methods of preparing amides, it would also appear that the above-described process, while best suited for unsubstituted amides, may not be the best method for substituted amides. In particular the direct ammonolysis of fats deserves close attention, as do the other methods briefly discussed below. Compounds of this class are very reactive and unit building blocks of

almost infinite variation can be made and are discussed in the patents. Many of the products are designated as emulsifiers and wetting agents, which could presumably have only a limited use in this respect as may be seen by their general structure. As a matter of record, some of the best detergents come from this group (Igepon T and 702K) but their sale in the United States last year did not represent 1% of the synthetics made, chiefly because of their price. These cost conditions could alter, of course.

The probability of an important new detergent emerging from the amides is not considered promising. This does not exclude possibilities of these materials, however, as detergent synergists to use in conjunction with soap or other synthetic materials.

The products of this class, as disclosed mainly by the patents, are, in general, waxy solids dispersible in water and showing surface activity. They are made without highly complicated apparatus, are far more stable than esters and are generally prepared from saturated acids, although the other acids work equally as well in many cases. The ability of this class of compounds to be built into extremely long and complicated patterns seems to indicate a wider field of use than emulsification or wetting, as promising as these fields appear to be at the present time. The vast increase in synthetic fibers will require more compounds for special treatments, such as creaseproofing, mothproofing, waterproofing, dyeing and filling. Although many of the amide derivatives are now directed toward these uses, particularly as textile softening agents, it appears that a large market awaits development, and the amide (and amine) type compounds present a most interesting field for research.

Many of these compounds are reported as high melting point waxes. It is not believed that the amides would be particularly adaptable to use as a wax substitute. The desire in this field is more for a straight chain acid from $C_{36} - C_{50}$, which would lead one to believe that the introduction of internal amide groups are detrimental for this purpose, just as branched chain acids interfere with detergency.

The possibilities for use as ore flotation agents appear promising, although the tendency in this field is toward using a rough classification with a cheap flotation agent and then to use an amide for the final classification. This procedure would greatly cut down the size of the available market. There are developments in the metallurgical field however for the recovery of very low grade materials where this market would be considerable because of the large tonnages involved. Mention has been made in the patent literature of the use of quaternary compounds for non-metallic ore flotation. These materials are not known to be in use commercially, although admittedly they have been metioned for this use.

The following very brief outline, indicates to some extent the nature of these products and the type of recent work being carried on. Actually, the simple equations below represent only the major reaction. In many cases complex groups of materials are obtained.

Preparation of Amides and Substituted Amides

1. Dehydration of the ammonium salt

$$RCOOH + NH_3 \longrightarrow RCONH_2 + H_2O$$

2. Dehydration of an organic amine salt

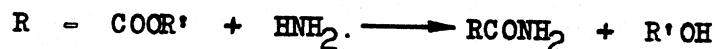$$R - COOH \cdot NH_2R' \longrightarrow R - CONHR' + H_2O$$
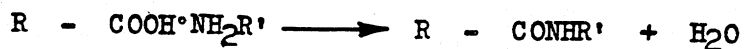
If an ethanolamine is used, the free hydroxyl group may be reacted further, or the free hydroxyl group may be displaced by alcoholysis with an ester. 2 Ethyl palmitate + ethanolamine $\longrightarrow$ palmitoylaminoethyl palmitate. This ester amide may be sulfonated (by chlorination followed by sodium sulfite treatment), oxyethylated with ethylene oxide, or treated with paraformaldehyde.

3. Reaction of fatty acids with aniline or urea.
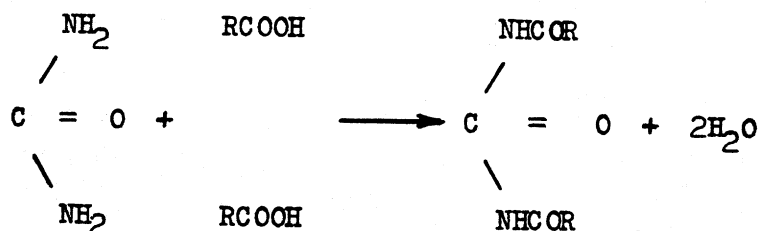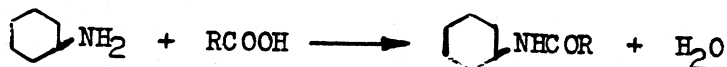
4. Reaction of amines with acid chlorides.

5. Ammonolysis of esters.

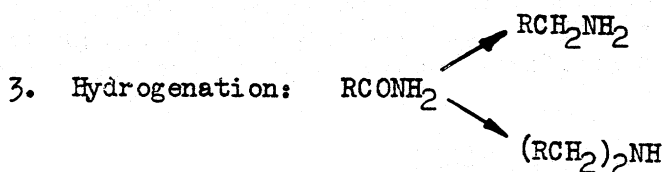$$R - COOR' + HNH_2 \longrightarrow RCONH_2 + R'OH$$
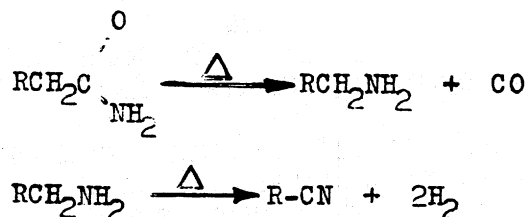
6. Hydrolysis of nitriles with acid.

$$RCN + H_2O \xrightarrow{H^+} RCONH_2$$

Typical Reactions of Amides

1. Hydrolysis: $RCONH_2 \longrightarrow RCOOH + NH_3$

2. Dehydration: $RCONH_2 \longrightarrow RCN + H_2O$

3. Hydrogenation: $RCONH_2$ 〈 RCH_2NH_2 / $(RCH_2)_2NH$
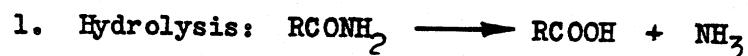
4. Dehydrogenation: Amide vapors are passed over Ni catalyst yielding
a nitrile and CO

$$RCH_2C\!\!\stackrel{O}{\underset{NH_2}{}} \xrightarrow{\Delta} RCH_2NH_2 + CO$$

$$RCH_2NH_2 \xrightarrow{\Delta} R\text{-}CN + 2H_2$$

5. Substitution by means of H_2S:

$$RCONH_2 + H_2S \longrightarrow RCSNH_2 + H_2O$$
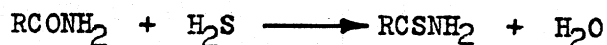
6. Substituted amides, $RCONHR'$

where R' =

(a) $-CH_2CH_2OH$, by reaction of amides with aldehydes. Also prepared
by reaction of fatty acids with ethanolamine.

(b) $-(CH_2CH_2O)_nCH_2CH_2OH$, by reaction of amides with ethylene oxide.

(c) $-SO_3H$, by reaction of amides with chlorosulfonic acid.

(d) $-CH_2CH_2OSO_3Na$

(e) $-CH_2CH_2SO_3H$, by reaction of amides with a chloroalkyl sulfonate or
by reaction of acid chlorides with taurine.

7. Substituted amides, $RCON\!\!\stackrel{R'}{\underset{R'}{}}$ '

where R' = R =

(a) $-CH_3$, by reaction of amides with dimethyl sulfate.

(b) $-CH_2CH_2OH$, by reaction of amides with ethylene oxide.

8. (a) Diamides, $R\text{-}CONH\text{-}R'\text{-}NHCOR$, by reaction of diamines with fatty acids.

(b) Diamides, $R\text{-}CO\underset{SO_3H}{N}\text{-}COR$

The stability of the resulting products in most cases permits many additional reactions to be carried out. For example, residual hydroxyl groups in the amides may be esterified, etherified, condensed with urea, sulfonated, etc.

TAURIDES ARE REPORTED TO IMPART A SLIPPERY FEEL TO DETERGENT SOLUTIONS. AMIDES ARE EMPLOYED IN THE MANUFACTURE OF EMULSIFIERS, GERMICIDAL EMULSIFIERS, ORE FLOTATION AGENTS, AND SHAMPOO THICKENING AGENTS. THE SUBSTITUTED AMIDE PREPARED BY THE DEHYDRATION OF MONOETHANOLAMINE LAURATE IS REPORTED TO BE A USEFUL ADDITION AGENT TO BAR SOAP. PATENTS HAVE ISSUED COVERING THE USE OF A DIAMIDE AS A CERAMIC LUBRICANT, AND RUST INHIBITOR, POLYAMIDES FROM DIAMINES AND MALONIC ACID ESTERS AS COATING MATERIALS AND AMIDES AS TEXTILE SOFTENERS, AND PLASTICIZERS.

WITH REGARD TO THE GENERAL UTILITY OF AMIDES FROM ANIMAL FATS, CONSIDERATION MUST BE GIVEN TO COMPETING MATERIALS. TALL OIL PRODUCTS ARE DEFINITELY IN THE PICTURE, BUT ITS TOTAL PRODUCTION IS LIMITED AND ALREADY ABSORBED. SHORT CHAIN AMIDES FROM HYDROCARBON SOURCES, AND AROMATIC ANILIDES ARE ALSO STRONG COMPETITORS, AS ARE THOSE FROM ROSIN. THE GENERAL REACTIVITY OF THE AMIDE GROUP MAKES IT POSSIBLE TO UTILIZE SHORT CHAIN MATERIALS TO PRODUCE DESIRED PRODUCTS IN COMPETITION WITH THE FATTY DERIVATIVES.

THE GREATEST OUTLETS FOR FATS IN THESE PRODUCTS TO DATE HAS BEEN IN THE FOLLOWING FIELDS:

EMULSIFIERS: MANY INTERESTING TYPES HAVE BEEN PREPARED FROM ANIMAL FATS AND NUMEROUS PATENTS HAVE BEEN OBTAINED. COMPETITION STEMS FROM SHORTER CHAIN AMINO AND AMIDO COMPOUNDS, AND FROM OTHER FAT AND NON-FAT DERIVED PRODUCTS. SUPERIORITY OF AMIDE TYPE PRODUCTS OVER THE ESTER TYPE IS IN THEIR GREATER ALKALI AND ACID STABILITY BUT THIS IS NOT ENOUGH TO WARRANT A VERY DECIDED PRICE ADVANTAGE IN MANY CASES.

DETERGENTS: THIS OUTLET IS CONFINED ALMOST EXCLUSIVELY TO IGEPON T. THIS PRODUCT CONSUMED LESS THAN ONE MILLION POUNDS OF FAT IN 1949. FACTORS WHICH HAVE LIMITED ITS USE ARE THE VARIABLE PRICE OF FAT, AND THE AVAILABILITY OF THE COUPLING AGENT (TAURINE). IGEPON T IS SLIGHTLY HYGROSCOPIC AND HAS NOT BEEN USED IN RETAIL PRODUCTS OF ANY NOTE. SUGGESTED RESEARCH WOULD BE ON MODIFIED ACIDS, IN PARTICULAR, DEHYDROCHLORINATED CHLOROSUBSTITUTED STEARIC ACID OR PRODUCTS OF SIMILAR NATURE.

QUATERNARY AMMONIUM SALTS: THESE ARE UNDERGOING A RAPIDLY EXPANDING FIELD OF USE AS GERMICIDAL AND BACTERICIDAL PRODUCTS. POTENCY IS SO HIGH, HOWEVER, THAT EVEN AN OPTIMISTIC FORECAST WOULD HARDLY PREDICT A DIVERSION OF MORE THAN 10 MILLION POUNDS OF FAT FOR THIS PURPOSE. OF TWENTY-SEVEN COMMERCIAL COMPOUNDS WHERE LENGTH OF ALKYL CHAIN WAS GIVEN, ONLY SIX ARE PREPARED FROM LONG CHAIN ACIDS, SUCH AS OLEIC OR STEARIC, THE BALANCE BEING CETYL, LAURYL OR MYRISTYL. FOR THE PURPOSE OF THIS INVESTIGATION RESEARCH ON ANIMAL FATS IN THIS FIELD DOES NOT APPEAR PARTICULARLY PROMISING.
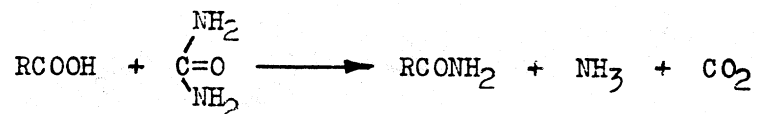
NITRILES

A number of methods exist for the preparation of the nitriles, most of which are of laboratory interest only due chiefly to the expensive reagents used, the type of raw material, etc. A few methods are worthy of further mention.

The main method of manufacture is the reaction of ammonia with fatty acids at elevated temperatures in either the liquid or vapor phase. The reaction may be simply explained on the formation of the ammonium soap and its dehydration, first to the amide and then to the nitrile.

$$R\text{-}COOH \ + \ NH_3 \ \xrightarrow{\Delta} \ R\text{-}COONH_4 \ \xrightarrow{-H_2O} \ RCONH_2 \ \xrightarrow{-H_2O} \ R\text{-}CN$$
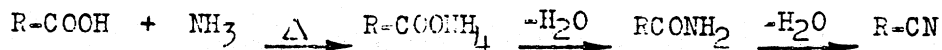
This equation is incomplete as it does not take into consideration the fact that pyrolysis of an amide also yields equimolecular amounts of both fatty acid and nitrile. The amide itself can be dehydrated to the nitrile by means of various agents, such as PCl_5, $SOCl_2$, P_2O_5, P_2S_5, P_2O_3, $COCl_2$, thoria, alumina, silica gel and aluminum phosphate. For the best yield of nitrile, the temperature should be above the decomposition point of the amide. For example, at low temperatures, the reaction of a fatty acid with urea or cyanuric acid gives the amide

$$RCOOH \ + \ \overset{\displaystyle NH_2}{\underset{\displaystyle NH_2}{C=O}} \ \longrightarrow \ RCONH_2 \ + \ NH_3 \ + \ CO_2$$

but at higher temperatures and under different conditions the same materials yield the nitrile. For long-chain fatty derivatives, nitrile is usually obtained between 400 - 450° C., although short-chain amides, such as sebacic diamide, may be dehydrated at 250° C. The removal of the water formed is also an assisting factor.

Should the demand arise, the nitriles (and amines) of the various fatty acids could be prepared, no doubt, in good purity and high yield either by using pure acids or by purification of the mixed nitriles. For economic reasons large tonnage usage will probably be largely confined to the use of mixed acids. Tall oil as a potential source of raw material for nitrile manufacturing must not be overlooked.

The fatty nitriles themselves have numerous uses. The C_{10} to C_{14} compounds have been mentioned in the literature for use as insect repellents, additives to lubricating oils to increase the lubricating qualities, ingredients in penetrating oil, additives to motor fuels, ore flotation agents, plasticizers for rubber, in the preparation of dinitriles, and in soap. The lower molecular weight derivatives have solvent properties. It is estimated that about 30 million pounds of fatty nitriles are produced per year.

The importance of the nitriles lies chiefly in the fact that they are the base for several large classes of products, namely, the amines and N-amides, and the quaternary ammonium compounds. Each class, including the nitriles themselves, gives rise to a host of derivatives so that the patent literature is full of references to new compounds the uses of which have been only touched on to date. Although the basic reactions of these materials have

been known for many years, some even dating back to the nineteenth century, the commercial availability has been limited almost entirely to the last decade.

Some Reactions of Nitriles

(1) Hydrogenation to the amine

$$RCN \xrightarrow[\text{cat.}]{H_2} RCH_2NH_2$$
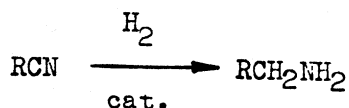
This reaction is the most important commercial reaction at present.

(2) Hydrolysis to the amide and the acid

This reaction is the least important from the commercial point of view, as it merely reverses the method of formation. The mechanism of the reaction indicates that it takes place in two steps, the hydrolysis of the nitrile to the amide and the hydrolysis of the amide to the acid. Under mild acid conditions the second reaction is fast, the first slow, but these rates gradually reverse as the concentration of acid is increased.

$$RCN + H_2O \xrightarrow{1st} RC\underset{NH_2}{\overset{\nearrow O}{}} + H_2O \xrightarrow{2nd} RC\underset{OH}{\overset{\nearrow O}{}} + NH_3$$
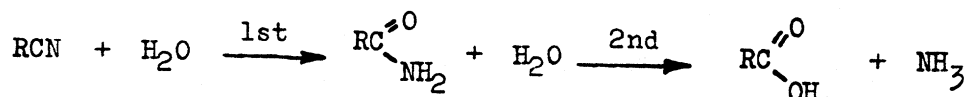
The higher the molecular weight, the more difficult is the hydrolysis and the more stable the product. Either acid, alkali or steam over a thorium oxide or aluminum oxide catalyst may be employed. Under proper conditions such as by the use of concentrated sulphuric acid, hydrolysis may proceed to the amide only.

(3) Reaction with alcohols

$$RCN + R'CH_2OH \xrightarrow[H_2O]{HCl} R-C\underset{OCH_2R'}{\overset{\nearrow O}{}} + NH_4Cl$$

(4) Thiohydrolysis
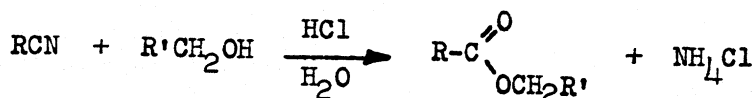
$$RCN + H_2S \xrightarrow[\text{alcohol}]{NH_3} RC\underset{NH_2}{\overset{\nearrow S}{}}$$
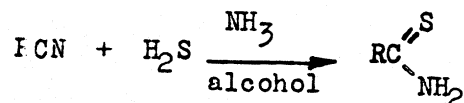
(5) Conversion to imino ether

$$RCN + R'OH + HCl \longrightarrow R-C\underset{OR'}{\overset{\nearrow NH \cdot HCl}{}}$$
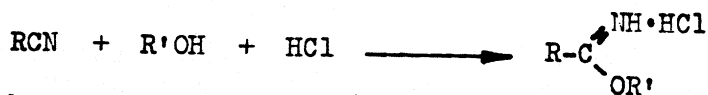
R'OH may be a phenol.

(6) Conversion to an aldehyde

$$RCN + HCl \longrightarrow RC \overset{NH}{\underset{Cl}{\diagdown}} \overset{H_2O}{\longrightarrow} R-C \overset{O}{\underset{H}{\diagup}}$$
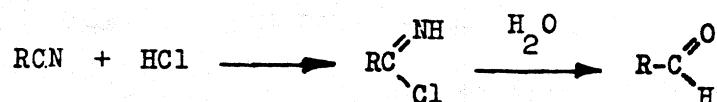
The intermediate iminochloride may also be hydrogenated. With the higher fatty nitriles, low yields are obtained.

(7) Conversion to ketones

$$RCN + R'MgX \longrightarrow \underset{R'}{R-C=NMgX} + 2HCl$$

$$\underset{R'}{R-C} = O + MgXCl$$
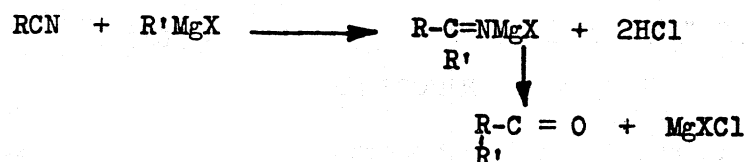
(8) Oxidation with H_2O_2

$$RCN + H_2O_2 \xrightarrow[40°C.]{alk.} R-C \overset{O}{\underset{NH_2}{\diagup}}$$
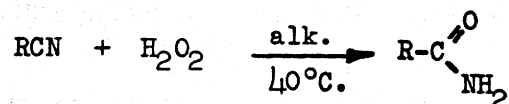
(9) Halogenation and dehalogenation

$$RCH_2CH_2CN + Br_2 \longrightarrow RCH_2CHBr \cdot CN \xrightarrow{alk.} RCH = CH-CN$$
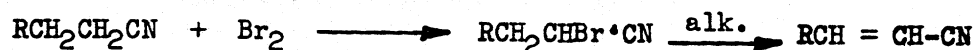
This product has a double bond and is very reactive as will be typified below. There is no specific information on the higher fatty nitriles but this reaction could be very promising depending on the ease and direction of halogen substitution compared with that of the acid or ester.

(10) Thermal cracking

Long chain nitriles are converted to short chain saturated and unsaturated ones, together with hydrocarbons. Since the short chain products are very reactive and in large demand as a base for syntheses, this reaction may be important.

(11) Conversion to amidoximes

$$RCN + NH_2OH \longrightarrow R-C \overset{NOH}{\underset{NH_2}{\diagup}}$$

(12) Condensation
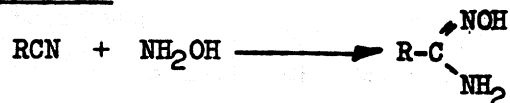
$$2RCH_2CN \xrightarrow{Na} RC(=NH)CHRCN$$
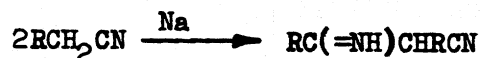
(13) Conversion to a diamide

$$RCN + R'COOH \longrightarrow R-C \overset{O}{\underset{\underset{O}{\overset{||}{NHC-R'}}}{\diagup}}$$
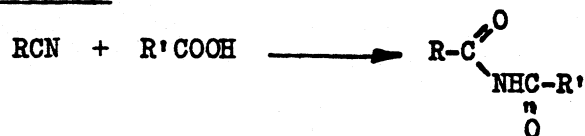
(14) <u>Reaction with alkyl iodides</u>

$$RCH_2CN + R'I \longrightarrow RR'CHCN \longrightarrow R(R')_2CCN$$
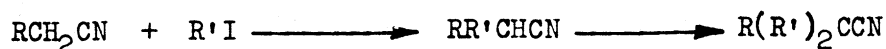
(15) <u>Conversion to an alkyl amidine</u>

$$RCN + R'NH_2 \longrightarrow R\overset{\overset{NH}{\|}}{-}C-NHR'$$
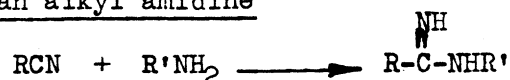
(16) <u>Conversion to amidines</u>

$$RCN + NH_3 \longrightarrow R-C\overset{NH}{\underset{NH_2}{<}}$$

(17) <u>Reaction with esters</u>

$$RCH_2CN + R'COOC_2H_5 \longrightarrow R\overset{COR'}{\underset{|}{C}}HCN$$
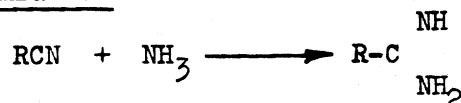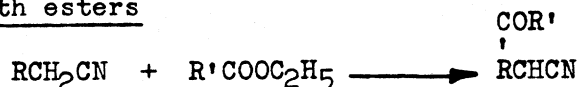
(18) The unsaturated nitriles undergo a wide variety of additions. These are available from natural sources, such as oleic nitrile, and also from reaction 9 above.

(a) $CH_2 = CH-CN + RNH_2 \longrightarrow RN\overset{}{\underset{R}{H}}CH_2-CH_2CN$

(b) $CH_2 = CHCN + Br_2 \longrightarrow CH_2Br-CHBrCN$

(c) $H_2S + 2(CH_2=CHCN) \longrightarrow S(CH_2-CH_2CN)_2$
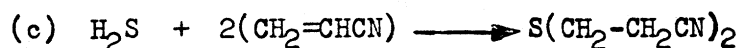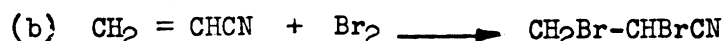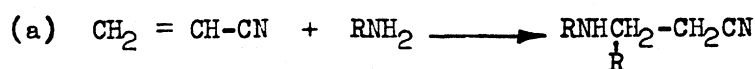
The above reactions are more or less standard for nitriles although a few may be more readily applicable to the short chain than the long chain nitriles. This list by no means attempts to cover all the types but does include those considered important to fat chemistry.

In regard to saturated fatty nitriles, particularly those from stearic and palmitic, reaction 9 above would appear interesting as a means of increasing their use. In the case of oleonitrile the double bond permits addition reactions, such as the formation of dimers and polymers followed by hydrolysis to polyunsaturated acids, or hydrogenation to polyamines.

When oleonitrile is subjected to vigorous oxidation, fission occurs as in the case of the free acid, yielding pelargonic acid and the seminitrile of azelaic acid in small yield. The addition of mercuric acetate to oleonitrile yields acetoxymercurimethoxystearonitrile, a useful weed killer.

THE NITRILES ARE CHIEFLY INTERMEDIATES WITH AMINES OR AMIDES AS END PRODUCTS. RESEARCH, THEREFORE, ON NITRILES WOULD NORMALLY BE DIRECTED TO REDUCE THE STEPS NECESSARY TO PROVIDE ONE OF THESE SECONDARY DERIVATIVES, OR TO STUDY METHODS OF MORE EFFICIENT PRODUCTION.

AMINES

The amines are secondary derivatives of fatty acids since they are formed by the low temperature hydrogenation of a nitrile which in turn is derived from a fatty acid by reaction of ammonia at high temperatures.

$$RCN \; + \; H_2 \longrightarrow RCH_2NH_2$$
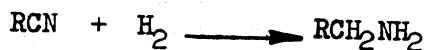
If hydrogenation proceeds much above $150°$ C. secondary fatty amines are formed through a complex series of intermediates, but which for simplicity may be considered as follows:

$$\begin{array}{c} RCN \\ + \; H_2 \longrightarrow \\ RCN \end{array} \qquad \begin{array}{c} RCH_2 \\ \diagdown \\ RCH_2 \diagup \end{array} NH \; + \; NH_3$$
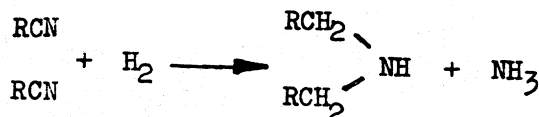
Since ammonia is formed during this reaction, conditions suppressing its formation enhance primary amine production, while venting the gases and using Ni catalyst favor secondary amine production.

The commercial formation of primary amines, therefore, by catalytic hydrogenation gives rise to secondary amines as an impurity. Similarly, secondary amines will contain primary as an impurity.

The primary saturated and unsaturated amines may also be formed from nitriles without secondary amine formation by the sodium reduction method where sodium is dispersed in toluene; and by many other methods which, at the moment, appear to have remote commercial importance as far as fatty acid derivatives are concerned because of the type of raw materials required and the costs involved in manufacture. In the case of the lower amines, this restriction does not apply and materials such as halides, aldehydes, esters and alcohols are readily available.

Some typical reactions for the preparation of amines are:

(1) The reaction of NH_3 with an alkyl halide

$$RCH_2Cl \; + \; NH_3 \longrightarrow RCH_2NH_2 \; + \; HCl$$
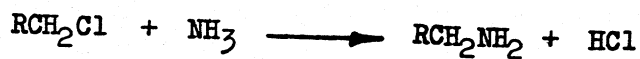
(2) The addition of NH_3 to an alcohol at high temperatures $(350°)$ in the presence of a dehydrating catalyst.

$$RCH_2OH \; + \; NH_3 \longrightarrow RCH_2NH_2 \; + \; H_2O$$
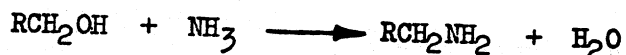
(3) The hydrogenation of aldehydes and ketones in presence of NH_3

(4) The hydrogenation of an amide at high pressures over Cu and Cr oxide catalysts.

The formation of primary amines from non-fat sources has some interest. Such amines are prepared from rosin-concentrated tall oil. Short-chain amines have been prepared from nitroparaffins. Chlorinated paraffins can be converted to amines with ammonia. As with most hydrocarbon sources, however,

the product formed has the disadvantage over fatty derived products in the uncertainty of composition, difficulties of separating isomers and the presence of branched chains. About 90% of those interviewed reported that there was no immediate concern over the Fischer-Tropsch and Oxo process as a source of fatty material. There appears little to warrant concern for the next five years, probably. On a long term basis, however, there is, and it is felt that the fat industry should be made aware of the danger involved in complacency toward basic research and unstable fat price. Short-chain synthetic acids are already reported to be superior to stearic acid in certain greases. Long-chain acids can be synthesized from ethylene, acetic acid and a benzoyl peroxide catalyst.

$$nCH_2 = CH_2 + CH_3COOH \xrightarrow[\substack{900 \text{ atmos.,} \\ 70 - 80°C.}]{\substack{\text{benzoyl} \\ \text{peroxide,}}} CH_3-(CH_2-CH_2)_n \; COOH$$

$$n = \text{about } 24$$
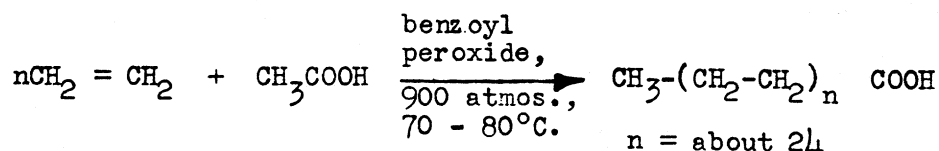
Considering ethylene at 2¢ per pound and acetic acid at 10¢ the ingredient cost of this operation would be just under 4¢ per pound for a C_{18} fatty acid, or under 3¢ for a C_{36} product. If any incentive were needed by the fat industry for a concerted effort on research, this process should provide it.

Secondary amines can be made by high temperature addition of NH_3 to the nitrile, by hydrogenation of amides at 260 - 280° over copper-chromium oxide catalyst with or without solvents, and from alcohols and low molecular weight amines.

$$RCH_2OH + R'CH_2NH_2 \longrightarrow \substack{RCH_2 \\ R'CH_2} NH + H_2O$$

No attempt is made here to depict the mechanism of the reaction. Secondary amines can also be made from primary amines by reaction with formaldehyde and formic acid.

$$RNH_2 + CH_2O + HCO_2H \longrightarrow RNHCH_3 + CO_2 + H_2O$$
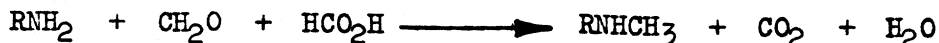
Tertiary amines may be formed, in general, from a secondary amine and an alkyl halide in liquid ammonia,

$$\substack{R \\ R} NH + R'Cl \longrightarrow \substack{R \\ R} N-R' + HCl$$

from a secondary amine and a primary alcohol,

$$\substack{R \\ R} NH + R'CH_2OH \longrightarrow \substack{R \\ R} N-CH_2R' + H_2O$$
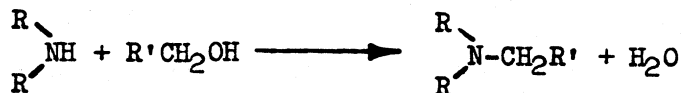
or by reacting formaldehyde and formic acid with a secondary amine

$$RR'NH + CH_2O + HCO_2H \longrightarrow RR'NCH_3 + CO_2 + H_2O$$
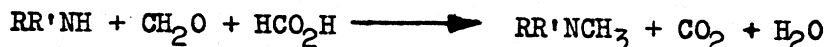
Attention must be drawn to a few special types of products to which the general methods above are applicable. For example, the dinitriles and polynitriles memtioned in the previous section can be converted to the di- and polyamines by methods similar to those used for mononitriles. Decarboxylation of certain N-substituted acids gives secondary amines.

$$R\text{-}CH\text{-}COOH \longrightarrow R\text{-}CH_2\text{-}NH\text{-}\bigcirc + CO_2$$

(with $NH\text{-}\bigcirc$ substituent below the CH)
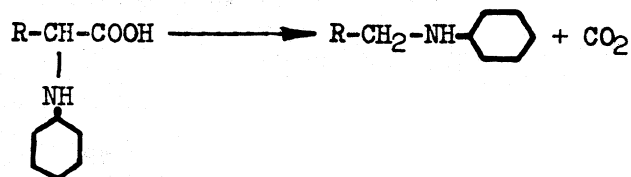
A STUDY OF THESE PROCESSES DOES NOT INDICATE A METHOD OF FORMATION OF COMMERCIAL IMPORTANCE OTHER THAN THOSE NOW EMPLOYED, NAMELY, THE HYDROGENATION OF NITRILES. ANY OTHER PROCEDURE INVOLVES THE USE OF ALCOHOL OR HALIDE, WHICH, WHILE FEASIBLE, IS RELATIVELY EXPENSIVE AND NOT COMMERCIALLY ATTRACTIVE BY METHODS NOW KNOWN.

Some Reactions of Amines

Practically all present production of commercial substituted amide detergents and emulsifiers are made by reaction of fatty acids with amines. The chief exception is Igepon T where the acid chloride instead of the acid is condensed with a substituted sulfonated amine.

The importance of the fatty amines does not lie in their potential use as detergent bases or emulsifiers but rather in the fact that they are cationic-type products which are substantive to fibers. They find their greatest use as substantive materials for fabrics where they can impart hand, creaseproofing, waterproofing, flameproofing, and other desirable characteristics. Because of the stability of the products and their versatile reactions they could become very important in plastics, paper, textiles and metal treating compounds.

The ready salt formation of the amines with easy dehydration to amides at temperatures close to the boiling point of water, formation of complex metal salts and of hydrates, eutectics and polymorphic forms, render these compounds particularly reactive.

The most interesting reaction is the addition of ethylene oxide. It is a powerful, relatively new, cheap tool for modifying the water solubility characteristics of long-chain organic derivatives in the emulsification and detergent field.

(a) Amine

$$RCH_2NH_2 + x\,CH_2CH_2(O) \longrightarrow RCH_2N \begin{cases} (CH_2CH_2O)_xCH_2CH_2OH \\ (CH_2CH_2O)_xCH_2CH_2OH \end{cases}$$

(b) Amide

$$RCONH_2 + x\,CH_2CH_2(O) \longrightarrow RCON \begin{cases} (CH_2CH_2O)_xCH_2CH_2OH \\ (CH_2CH_2O)_xCH_2CH_2OH \end{cases}$$
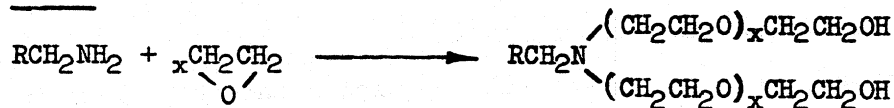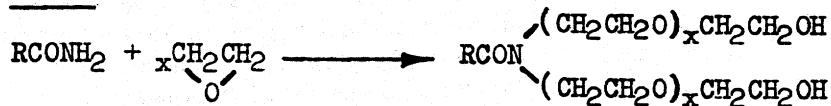
The reaction products of long-chain amines with ethylene oxide are cationic in varying degrees, becoming more nonionic as the moles of ethylene oxide increase. Since detergency requires the material to be in a colloidal state, increased water solubility through the addition of too many moles of ethylene oxide has an adverse effect. Stearylamine has its best surface tension with 5 moles of ethylene oxide, best wetting time with 10 moles.

Amines also react with CO_2 and CS_2 yielding carbamates, thiocarbamates, dialkyl ureas and alkyl isothiocyanates.

$$RNH_2 \quad + CS_2 \longrightarrow \overset{\nearrow SH \cdot H_2NR}{\underset{\searrow NHR}{C=S}} \xrightarrow{\text{(heat)}} \overset{\nearrow HNR}{\underset{\searrow HNR}{C=S}} + H_2S$$

Dialkylthiourea

$$\longrightarrow RNH_2 + RNCS + H_2S$$

Alkyl isothiocyanate
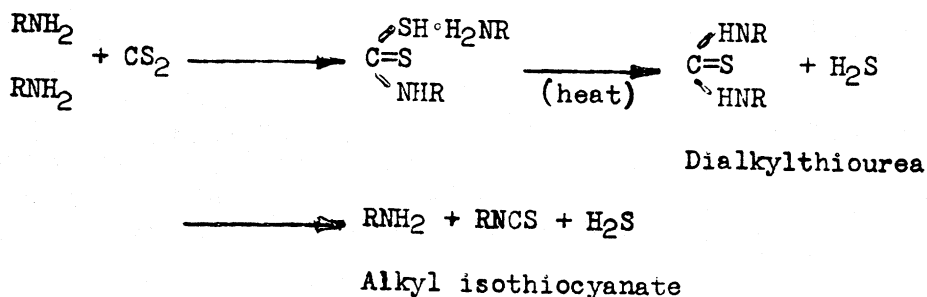
Amines yield olefines, mainly, when heated with a dehydrating catalyst such as $ZnCl_2$ or H_3PO_4. These reactions are not interesting commercially.

Other reactions include sulfonation, oxidation, nitrite formation, and addition to unsaturated esters, such as acrylates.

Principal uses of fatty amines and amine salts to date:

(1) Non-metallic ore flotation for the separation of calcium phosphate and carbonates from silica, KCl from NaCl.

(2) Bactericides

(3) Emulsifiers

(4) Waterproofing cement

(5) Insect repellents

(6) Dyeing

(7) In enamels, lime, etc.

(8) In water clarification

(9) Rust inhibitors in lubricating oils

The short chain amines are still basic building blocks and it will probably be some time before the C_{12} - C_{18} chains are able to be used in the same manner that the C_4 and C_6 are being used at present. Large tonnage use of the long-chain amines will be developed only when these are used as units in far more complicated products than have been developed to-date, where their long-chain structure will prove superior to petroleum derivatives.

For the same reasoning as above, the secondary symmetrical long-chain amines are less interesting than the primary, and the tertiary less than the secondary. This does not include the unsymmetrical tertiary amines used extensively as textile softening agents or the unsymmetrical quaternary ammonium compounds widely made and used not only as textile softening agents but for waterproofing as well.

THE AMINES AND AMIDES FORM THE MOST INTERESTING CLASS OF FAT DERIVATIVES BECAUSE OF THE MANY TYPES OF REACTIONS POSSIBLE. THE SHORT-CHAIN, NON-FATTY AMINES ARE COMPETITORS OF THOSE WHICH ARE FAT DERIVED, AND IN MANY USES THE FATTY AMINE IS PRESENT IN MINOR PROPORTION. ALTHOUGH RESEARCH IN SUCH A DIVERSE FIELD IS BOUND TO BE PRODUCTIVE OF NEW PRODUCTS AND USES, SUCH USES WOULD LARGELY BE SPECIALIZED PRODUCTS HAVING SMALL TO MODERATE TONNAGE VOLUME, WHICH IN TOTAL COULD ASSUME A FAIRLY LARGE TONNAGE. THIS OPINION IS BASED ON AN EXAMINATION OF THE PATENT STRUCTURE IN THIS FIELD PLUS THE OPINIONS EXPRESSED IN THE COURSE OF THE SURVEY.

IT IS IMPOSSIBLE TO ESTIMATE, HOWEVER, WHEN A SINGLE PRODUCT OR TYPE OF PRODUCT WILL BLOSSOM INTO AN UNPREDICTED USE OF LARGE VOLUME. THE LONG-CHAIN AMINE SALTS, USED IN ORE FLOTATION, ARE JUST SUCH A CLASS. THEIR PRESENT RATE OF CONSUMPTION IN THIS FIELD IS ESTIMATED AT OVER 150,000 POUNDS PER YEAR, WITH A POTENTIAL USAGE OF 4 TO 5 MILLION POUNDS PER YEAR.

IT IS SUGGESTED THAT RESEARCH IN THIS INTERESTING FIELD BE APPROACHED FROM A DIFFERENT VIEWPOINT THAN APPEARS TO HAVE BEEN THE CASE TO DATE. IN ORDER TO ESTABLISH THE PRODUCT BEYOND THE REACH OF COMPETITIVE MATERIALS, THE PRODUCT MUST UTILIZE THE NATURAL PROPERTIES OF THE BASE UNITS TO THE GREATEST EXTENT. IN THE CASE OF THE FATTY AMINES AND AMIDES (SINCE THE DERIVATIVES OVERLAP) THESE SEEM TO BE TWO FOLD.

(1) THE NORMAL FATTY CHAIN WILL ADD WATER INSOLUBILITY, RESILIENCE AND PLASTIC QUALITIES TO A PRODUCT.

(2) THE PRODUCTS ARE, OR CAN BE MADE, CATIONIC.

IN CASE 1, INVESTIGATION WOULD PROCEED ALONG THE LINES OF MAKING THE FATTY RADICLE A CHEMICAL ADDITION PRODUCT TO OTHER PRODUCTS USED IN LARGE TONNAGE, FOR EXAMPLE, PLASTICS, SYNTHETIC TEXTILE FIBERS, PLASTICIZERS, CELLULOSE AND PAINTS. THE STRENGTH OF THE N BOND WOULD MAKE SUCH BUILT IN RADICLES SUPERIOR TO THE ESTER GROUP, ALTHOUGH IT IS QUITE CONCEIVABLE THAT THE ESTER COUPLING WOULD BE DESIRABLE ON OCCASION.

THIS PROPERTY OF THE QUATERNARY DERIVATIVES OF BEING SUBSTANTIVE TO MANY FIBERS HAS BEEN THE ONE MOST EXTENSIVELY EXPLOITED TO DATE IN TEXTILE APPLICATION.

ALCOHOLS

These are commercially available. A large outlet is the sulfate ester employed in detergents. In the largest selling synthetic detergent in America, it is estimated that between 50 and 60 million pounds of fat (as alcohol sulfate) are consumed in its manufacture each year. Prior to 1946, alcohol derived synthetic detergents were being made exclusively from cocoanut oil

alcohols. Recently an increasing amount of tallow has been used. Tallow might be substituted up to 50% of coconut oil. On a basis of a 50/50 split, approximately 25 to 30 million pounds of tallow would be converted to alcohols for sulfation in 1949. To this add 10 million pounds for other industrial uses, and an estimated 35 to 40 million pounds may have been produced. Total fats going to produce alcohols from all sources then is estimated at approximately 70 million pounds.

Many patents have been taken out on methods of production although only three commercial methods are in use:

   (1) The sodium reduction method. Yields are about 87%. This process is applied directly to the glycerides.

   (2) High pressure hydrogenation of glycerides over a copper-chromium oxide catalyst.

   (3) High pressure hydrogenation of fatty acids. Some interest has recently been expressed in the high pressure (4000 psi) reduction of the heavy metal salts. Temperatures range from 240 to 400° without excess hydrocarbon formation. This process warrants close attention.

A number of laboratory methods also exist.

The most important reaction product of the alcohols is their acid sulfate ester, formed when concentrated sulphuric, or preferably chlorosulfonic acid is caused to react with the alcohol.

$$RCH_2OH \ + \ H_2SO_4 \longrightarrow RCH_2OSO_3H \ + \ H_2O$$
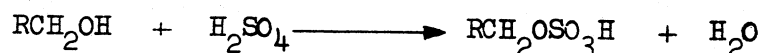
The neutralized acid ester is employed in detergent formulations. Generally, the Na salt is used, but the organic salts, such as the triethanolamine salt for high lathering shampoo base materials, are also made. Industrial products are sometimes neutralized with potassium or ammonium hydroxide. Other reactions include the formation of dialkyl sulfates by the conversion of the alcohol to an alcoholate and reacting this with an alkyl chlorosulfonate, the formation of phosphoric acid esters, useful as plasticizers, the decomposition of an alcohol to an olefin through dehydration at elevated temperatures in the presence of an activated aluminum oxide or similar dehydrating catalyst, and the dehydrogenation of an alcohol at elevated temperatures in the presence of a metallic catalyst, such as Ni or Cu, to yield a heterogeneous mixture of olefins and aldehydes. Of some interest is the reaction in which the alcohol gives up its hydrogen to an olefin and is converted into an aldehyde.

$$RCH_2OH \ + \ -CH = CH- \longrightarrow RC\overset{O}{\underset{H}{\diagdown}} + \ -CH_2-CH_2-$$
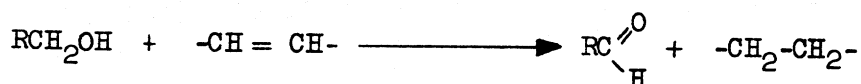
Ethylene oxide adds to alcohols to produce emulsifiers having considerable use in industry. Some uses of alcohols, other than in detergent formulations, are as follows:

(1)   Sulfoacetic acid ester of (a) lauryl alcohol as a wetting and anti-spattering agent, and (b) octyl alcohol as an anti-spattering agent and for ore flotation.

(2)   Oleyl alcohol ester of a short chain unsaturated acid, as in additive to mineral oils.

(3)   Oleyl phthalate as an antigumming agent in oils.

(4)   Air-blown oleyl alcohol, for textile use.

(5)   Fatty alcohol sulphates in soap.

THE USE OF THE HEAVY METAL SALTS FOR ALCOHOL PRODUCTION IS VERY INTERESTING AND SHOULD BE WATCHED. FURTHER EXPANSION OF TALLOW INTO THE SYNTHETIC DETERGENT FIELD TO REPLACE AN ADDITIONAL 25 MILLION POUNDS OF COCONUT OIL IS A POSSIBILITY. THE ALCOHOL SULFATE DETERGENTS ARE EXCELLENT, AND PRICE ALONE IS THE DRAWBACK COMPARED TO THE ALKYL ARYL SULFONATES. IT IS ESTIMATED THAT 13¢ ALKYL ARYL SULFONATE (40% ACTIVE) IS EQUIVALENT IN VALUE TO THE ALCOHOL SULFATE WHEN THE LATTER IS PRODUCED FROM 7¢ RAW MATERIALS.

MISCELLANEOUS

The aliphatic chlorides, anhydrides, aldehydes, ketones, ethers, sulfides, mercaptans are relatively unimportant commercially, although a great many laboratory reactions are described. The chloride is used for special condensations. Long chain ketones can be made by heating the calcium salts of the fatty acids or by heating the acids at 300 - 350° in the presence of a reduced iron catalyst. The ketone can be reduced to a secondary alcohol and sulfated to yield a wetting agent.

Chain Modification

DOUBLE BOND ISOMERIZATION

Elaidinization, double bond shift reactions, and conjugation, etc. are unimportant commerically at the present time with regard to animal fats. Double bond shifts are extremely important in drying oils, however.

ADDITION REACTIONS

Hydrogen addition is the most important. Since oils do not require acid resisting material, do not readily poison the catalysts and reduce under normal pressures, the acids are hydrogenated only in special cases where the oil is not available or where the acids are cheaper, such as acidulated soap stocks.

Halogen addition to the acids is of more theoretical than practical interest. The dehydrochlorination of acids gives a mixture of conjugated and non-conjugated acids whose pentaerythritol esters are suitable as drying oils. It is questionable, whether such a process applied to animal fats could compete with vegetable drying oils and derivatives.

The double bond of oleic acid is an important opening in the molecule for the addition of many modifying groups, such as aryl, by means of Friedel-Crafts catalysts, the sulfate or sulfonate, to increase wetting power, and hydroxy groups added by means of hydration or partial oxidation. The double bond in oleic acid (or its esters) provides a ready means of making a complete new series of substituted stearic acids (or esters), such as the dihydroxy-stearic and epoxystearic acids by hydrogen peroxide oxidation. These deriva-tives are useful as plasticizers, solvents and intermediates.

FISSION OF OLEIC ACID

Fission products are among the most interesting derivatives of oleic acid. Oleic acid yields, mainly, two products which have considerable use, pelar-gonic acid, very useful as a plasticizer in vinyl resins when esterified, and azelaic acid which displays many of the reactions and uses of adipic and sebacic acids. The polyamides prepared from azelaic acid and polymethylene diamines have fiber possibilities. The esters of dibasic acids are useful also as lubricants and plasticizers.

A commercial method for cleaving oleic acid is oxidation with dichromate with subsequent regeneration of the spent chromium sulphate by electrolysis. The hydrogen generated during electrolysis is used to harden more stock. The yield of products is believed to be approximately 80%. Only recently an announcement of cleavage by ozonization has been made.

Nitric acid has been mentioned as a cleavage reagent, but it is reportedly too drastic and gives too many side reactions. Potassium permanganate is too expensive. Air oxidation is probably the most interesting. The fission does not proceed as one might normally expect nor are high yields of fission products obtained by present techniques due to the formation of by-products. Peroxides are formed first, with fission occurring on either side of the 9 - 10 bond. The intermediate hydroperoxides are claimed to be soap stabilizers.

FISSION OF SATURATED ACIDS (STEARIC AND PALMITIC)

Fission products from the saturated acids have been relatively neglected. Generally, degradation products are uneconomical since the multitude of by-products formed are of little or no value, and the shorter chain products are available more cheaply from petroleum chemicals.

Saturated acids may be made to undergo oxidation with the formation of various degradation products. Generally speaking the α-carbon is attacked first giving rise to shorter chain acids. The activity of the α-carbon de-creases with increased chain length so that by the time stearic acid is reached only vigorous oxidizing methods can attack the chain at all. This minimizes any slight directional forces that may be present, and results in mixtures of degradation products which are not attractive economically. For example, the loss in weight alone through degrading stearic to palmitic acid, were it possible to so regulate the reaction, would represent a loss of 9% material

and, at 15¢ for stearic, would make palmitic cost 16-1/2¢. For the same reason, myristic would cost 18.7¢ and lauric 21.3¢. This cost is for basic material alone without adding the cost of oxidation, or fractional distillation, etc. By the time lauric acid were reached in any oxidation procedure, large quantities of lower acids would be formed so that losses from such sources would also have to be added to the costs. There is no point in speculating further on the costs of such procedure since research to date has not shown any practical way of accomplishing this purpose. Actually the cost ratio of coconut oil to tallow would have to be in the neighborhood of 2:1 before it would be feasible even to initiate serious research for this purpose. The same reasoning applies to nitric acid oxidation where the degradation products are chiefly the dibasic acids.

Some evidence exists that low temperature oxidation of the saturated acids can be made to yield hydroperoxides with the end product mainly ketones plus some alcohols

$$-CH_2-CH_2-CH_2- \xrightarrow{O_2} \underset{\underset{OOH}{|}}{-CH_2-CH-CH_2-} \longrightarrow \underset{\underset{O}{\|}}{-CH_2-C-CH_2-}$$
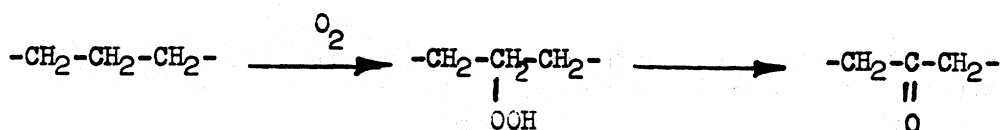
but the importance of this reaction as a commercial source of material is slender until the mechanism of the reaction has been more thoroughly studied so that the reaction can be controlled to give high yields of desirable products.

A promising reaction is hydrogen peroxide oxidation of the ammonium salts of the higher acids to yield β-keto acids.

$$RCH_2CH_2COOH \xrightarrow{H_2O_2} RCOCH_2COOH \longrightarrow RCOCH_3 + CO_2$$
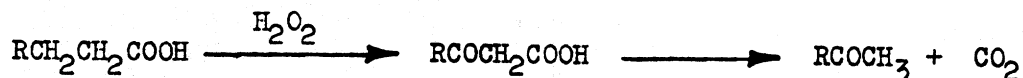
The reactivity of the ketone, plus the fact that only one carbon is lost, suggest that the reaction be investigated further.

Fission products by pyrolysis of saturated acids are unimportant as a commercial source of new materials, since the products obtained are obtainable more easily from petroleum sources. The bombardment of saturated acids with α particles results in decarboxylation and has only theoretical interest. α-Bombardment by use of radium does not cause any measurable elaidinization of oleic acid at room temperatures over several months of contact.

SUBSTITUTION PRODUCTS

Chlorine, being the cheapest halogen, is the most important substituting agent, at present. Saturated acids generally are believed to substitute first on the α-carbon. Once a halogen has entered, however, subsequent halogenation proceeds more rapidly with substitution taking place at random along the entire chain. The maximun substitution practical on a commercial scale is about 5. Above this, the chlorinated compound becomes unstable, and such products have a limited use. The carboxyl group is usually protected by conversion to the methyl ester. Methyl pentachlorostearate is a

plasticizer. It must be prepared from extremely pure stearic to avoid dis-
coloration and for such purposes the triple pressed grade of stearic acid
is used. Methyl dichlorostearate is also made commercially for use as an
oil additive. Production of both types of products (dichloro and pentachloro)
consumes approximately 200,000 pounds of stearic acid per year, the penta-
chloro product being the more important one.

The data on the salts and other esters of such chloro products were not
available but it is felt that the use, while having good possibilities of
increasing, will not consume very large quantities of stearic or palmitic
acid.

Of more interest is the use of chlorine in increasing the solubility of
stearic acid salts for soap use. Sodium stearate is a soap of low solubility,
which to some degree accounts for the large use of coconut oil in the soap
industry. Chlorine does not enter the α position of a stearic or palmitic
ester with the same directional ease as does bromine. The reaction of α-
chlorostearic acid with alkanolamines is of interest. Since the halogen is
lost in the reaction and since bromine is approximately five times the cost
of chlorine (pound for pound) and ten times its cost on a molar basis, the
latter material would be the only halogen practical in any present day large
scale commercial use, irrespective of its non-directional qualities. Deriva-
tives, through the bromo component, would be restricted to special products.
Other common means are available for replacing the chlorine with a water
solubilizing group, such as hydroxyl, by means of alcoholic potash. α-
Dicarboxylic acids can be prepared by replacing the halogen with cyano
followed by hydrolysis.

$$R-CHBr-COOH \xrightarrow{\text{KCN}} \underset{\underset{CN}{|}}{R-CH-COOH} \xrightarrow{\text{H}_2\text{O}} \underset{\underset{COOH}{|}}{R-CH-COOH}$$
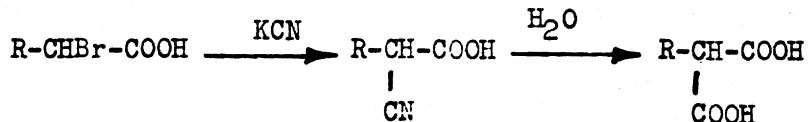
Dehydrochlorirating over a cobalt chloride-pumice catalyst at 220-280° at
reduced pressure gives high yields of unsaturated products from dichloro-
stearic and dichloropalmitic acids containing from 0.7 to 8.4% residual
chlorine, 2.6 - 6.7% unsaponifiable, less than 0.2% saturated acids and iodine
values from 130.2 to 157.7. The ester is harder to dehydrohalogenate than
the acid, a factor not influenced by halide position. The soaps produced
have far greater foam power than coconut or oleic acid soaps and greater
wetting power than sodium oleate or sodium dodecylbenzenesulfonate.

Three factors are believed essential to make this process a satisfactory
method of improving stearic and palmitic acid for soap use.

    (1) Improvement in yields. Since the experiments described were con-
ducted only in a laboratory and pilot plant this problem would probably be
one of plant design.

    (2) Reduction of residual chlorine. This might be bothersome in a
finished product and cause discoloration. Values in the range of 0.2% might
be satisfactory.

    (3) The double bonds introduced might be detrimental. The usual ex-
perience of soap makers is that unsaturation tends to cause rancidity and
off coloration.

Only a slightly increased solubility of stearic and palmitic acids would be required to make them equivalent to $C_{12} - C_{14}$ acids.

An examination of costs on a two step, 20-ton per day plant capitalized at \$20 per ton year of production would be as follows: (Costs estimated by J. W. McCutcheon).

1210* lb.	Hydrogenated tallow at 8-3/4¢ + 1¢ for hydrogenation and splitting	\$118.00
293 "	Chlorine at 4.4¢	12.90
	Catalyst (est.)	.04
	Steam power and water	.59
	Labor at \$2.00 per hour	2.40
	Overhead (100% of direct labor)	2.40
	Amortization of plant (10 years)	1.00
	Repair and Maintenance	.20
		\$137.53

Present (July, 1951) cost of tallow 8-3/4¢; coconut oil 12-1/2¢
Estimated cost of derivative 13.75¢ perpound (yield 1000 lbs.)
Efficiency of product 114% of coconut oil soap
Cost of derivative in terms of equivalent detergent power of a coconut oil soap - $100 \times \frac{13.75}{114} = 12$¢

* Weight of fat to yield 1150 pounds of acids for 88% yield of product.

In commercial operation the tallow would probably be continuously split, partially separated by solvent extraction or crystallization, the concentrated stearic run through the chlorinator and dehydrochlorinator and reunited with the red oil.

An examination of this or similar processes indicates possibilities in the following directions:

(1) Reduction of the amount of coconut oil in soap. Present consumption of coconut oil is approximately 300 - 400 million pounds per year. This would be a large tonnage outlet possibility for tallow.

(2) Substitution of tallow in present fat based alcohol sulfates. The estimated amount involved is 25 million pounds.

a-Chloro substituted fatty acids also react with amines. On the basis of 4.4¢ per pound chlorine, an estimated cost of producing a monoethanolamine derivative using such equipment as an (1) esterification kettle, (2) chlorinator, (3) dehalogenator and (4) saponifier with alcohol recovery is considerable and could only be done on a large scale and with continuous equipment. Since the alcohol is recoverable and the additive forms a part of the product, cost of the process depends largely on the cost of the halogen versus utility of product. Since solubilization is only one phase of the problem of utilizing stearic acid in soaps, the cost of production is still out of line with other competitive fat sources, such as coconut oil; and probably indicates why so little work has been done on such research. One point worth

consideration in such a study, however, and mentioned previously is the fact that a small percentage of a more soluble soap often has a tremendous general effect on the product. A small amount of mysristic or lauric acid soaps, for example, have a great influence on the solubilization of stearic acid soaps. For this reason it is quite possible that only a partial conversion to a soluble stearate would be necessary.

Any large-scale application of this process would involve the use of a cheaper raw material than stearic acid. Since chlorine adds readily at the double bond before it would substitute, tallow would not be suitable unless it were hydrogenated at a cost of 1¢ - 1-1/4¢ or fractionally separated by solvent extraction, crystallization and/or interesterification methods. These last methods are commercially available and could very well supply a raw material at a price within 2¢ of the market.

The discussion to this point has covered only substitution when the carboxyl group is blocked. When the acid itself is halogenated with bromine in the presence of red phosphorus as a catalyst, substitution occurs both at the α-position and at the carboxyl group. Palmitic acid gives α-bromo palmitoyl bromide.

TWO METHODS HAVE BEEN SUGGESTED FOR IMPROVING STEARIC ACID OR TALLOW FOR DETERGENT AND OTHER USES. THE MOST PROMISING ONE INVOLVES CHLORINATION AND DEHYDROCHLORINATION. COSTS HAVE BEEN ESTIMATED ON SUCH A PROCEDURE AND ARE NOT EXCESSIVE WITH PRESENT RAW MATERIAL PRICES.

SECTION 3

EDIBLE ANIMAL FAT PRODUCTS

STATISTICS

Table 7 below gives a brief summary of edible fat production and consumption for the period 1936 to 1949 as given by the Bureau of the Census. As pointed out by Department of Commerce, large quantities of lard and tallow are produced locally and are not included in these figures. However, the data will be comparable to those given for inedible fats.

TABLE 7

FACTORY PRODUCTION & CONSUMPTION (IN 1,000'S OF POUNDS)*

YEAR	RENDERED LARD (INCLUDING NEUTRAL LARD AND RENDERED PORK FAT)		EDIBLE TALLOW	
	PRODUCTION	INEDIBLE CONSUMPTION	PRODUCTION	INEDIBLE CONSUMPTION
1936	1,063,155	77	96,117	564
1937	896,474	207	78,144	857
1938	1,163,142	23	93,481	891
1939	1,413,751	80	95,825	1,864
1940	1,686,097	789	78,702	2,269
1941	1,622,989	91	91,139	6,766
1942	1,894,411	338	111,872	1,571
1943	2,163,410	88,347 (2)	130,804	5,298
1944	2,443,276	184,119 (2)	102,943	44,989 (3)
1945	1,315,523	82,416 (2)	114,735	33,412 (3)
1946	1,408,271	1,156	71,572	7,631
1947	1,781,308	7,472	94,985	8,070
1948	1,791,446	5,030	69,713	3,264
1949	2,184,000	(1)	105,562	(1)

* U. S. Bureau of the Census Data
(1) Not available
(2) Principally to soap use as follows: 1943-74,038, 1944-176,266 and 1945-82,070.
(3) Principally to soap use as follows: 1944-43761, 1945-32,067.

These data show the comparatively small production of edible tallow compared to lard, in all cases below 10% and in a few cases below 5%. The question of increasing the edible tallow production was considered in the survey. The opinion was that the present scale of production between edible and inedible tallow was in balance with the differential of about 1¢ in price between the two. Edible tallow has a greater stearin content than lard and finds its greatest use in shortening.

Without attempting at this point to discuss edible consumption, which figures will be given in Table 8 to follow, a total figure showing how much fat was diverted from edible to inedible use is included in Table 7. Except for the war years 1943-4-5 when large quantities of both materials were diverted to soap use (see footnote to Table 7) the total diversion is insignificant. We could leave this point, therefore were it not for the fact that during 1950 considerable quantities of edible fats up to an estimated 100 million pounds was used in soap. During the last quarter of 1950, 60 million lbs. of edible animal fats were diverted to soap. This abnormal diversion is attributed to the soft price of lard during this period as compared to grease and to the fact that there has been a gradual shift from tallow to grease, during and subsequent to the war.

Any shift however from hard to soft fats in soap or from inedible grease to lard, does not affect the overall animal fat situation since one animal fat merely replaces another animal fat.

The main uses to which edible animal fats are put are in

(1) shortening
(2) margarine
(3) mayonnaise
(4) salad dressings
(5) bakery goods
(6) confectionery
(7) commercial roasting
and frying

Table 8 illustrates this point.

TABLE 8*

Factory Consumption of Lard in
Edible Products.   (In 1000's of pounds)

Year	Total	Shortening	Oleomargarine	Other Edible Products
1936	7,318	4,503	2,198	471
1937	8,938	915	1,747	6,013
1938	9,925	2,925	1,464	5,518
1939	15,253	7,398	1,355	6,317
1940	29,519	16,786	5,098	6,587
1941	18,606	5,237	8,298	4,724
1942	51,221	30,094	8,134	7,999
1943	144,728	36,407	11,694	3,166
1944	243,738	38,729	9,631	3,166
1945	115,467	23,142	5,787	3,372
1946	29,172	20,387	2,058	4,781
1947	114,971	100,635	3,144	3,720
1948	125,870	113,996	3,498	3,346
1949	130,133	88,475	(1)	2,758

* U.S. Bureau of the Census reports
(1) Not available.

This table indicates that the factory consumption of lard in shortening is increasing appreciably. Only during the war years did any significant amount of lard go into oleomargarine. The use of lard in other edible products is insignificant and the amount used has been steadily diminishing since 1937.

There is some consideration being given to the use of fat to supplement cat and dog food preparations. These must be considered as a non-edible fat outlet and are so classified by the Bureau of the Census (Animal and Vegetable Fats and Oils 1945-1949 P65). Efficient extraction methods have reduced the fat in many protein feed materials such as cracklings from a normal 7 to 8% by pressing or expeller means to about 2-3% or even lower by extraction means. This latter process is presently estimated to account for about 10% or 200 million pounds per year of the total production of grease and tallow.

The reduction of fat content in extracted feed materials has reached a point where some additional fat or carbohydrates may be required. This problem is under study, particularly the advantage of a fat over carbohydrate addition to the feed, since carbohydrates usually cost less than fats on a caloric basis. The market is surprisingly large. Dog foods average about 5% fat content and are classified roughly as dry dog foods (4-5% fat content) and wet or canned dog foods (5-6% fat on a dry basis). Sales of dry dog foods exceed those of wet dog foods. Bureau of Census data for 1947 give dry cat and dog food production at 680,712,000 pounds valued at $57,970,000, and wet cat and dog food at 427,137,000 pounds valued at $38,389,000. Present estimates place wet dog food production at 1,000,000,000 pounds valued at $75,000,000 with the value of the dry product placed at $125,000,000. On the basis of the 1947 production of dry cat and dog food (680,712,000 pounds) and a 4% fat content, then an increase to 15% fat content would require an additional use of 75 million pounds of fat per year. Broiler poultry feeds contain about 3-1/2% fat. An increase to 5-1/2% would also represent a usage of 75 million pounds of fat on the present consumption basis. All poultry feeds, including broiler feeds contain about 3% fat. An increase of 1% fat content to 4% would represent an increased usage of fat up to 340 million pounds.

The above avenue of investigation is interesting, but physiological evidence would have to be forthcoming to establish that fat addition is superior to carbohydrate under the conditions of use. Furthermore, it is necessary to consider only that portion of fat in excess of past usage as supplying a new outlet. For example, if cracklings are reduced from 7 to 3% fat content and then the cracklings have to be fortified with 4% fat to bring them up to a feed standard, the 4% fat added cannot be considered a new outlet.

Referring again to Table 8, it should be noted that the usage of lard in shortening has been steadily climbing. This is due chiefly to the compounded lard products now being placed on the market by the large packers. Table 9 shows the relation between butter, shortening, lard, margarine and miscellaneous edible oils such as salad oils, roasting fats, etc.

TABLE 9*

Civilian Consumption (pounds)

Year	Butter Fat (2)		Lard		Margarine		Shortening		Edible Oils		Total	
	Millions	Per Capita	Millions	Per Capita	Millions	Per Capita	Millions	Per Capita	Millions	Per Capita	Millions	Per Capita
1936	1701	13.2	1442	11.2	322	2.5	1580	12.3	732	5.7	5757	44.8
1937	1706	13.2	1358	10.8	326	2.5	1589	12.3	818	6.3	5796	44.7
1938	1729	13.2	1436	11.0	312	2.4	1499	11.5	890	6.8	6866	44.9
1939	1832	13.9	1662	12.6	243	1.8	1396	10.6	946	7.2	6079	46.2
1940	1806	13.6	1901	14.3	256	1.9	1185	8.9	997	7.5	6145	46.3
1941	1702	12.9	1819	13.7	294	2.2	1368	10.5	1100	8.3	6283	47.1
1942	1685	12.7	1689	12.8	296	2.2	1237	9.3	1001	7.6	5907	44.6
1943	1228	9.5	1678	13.0	408	3.1	1234	9.5	848	6.5	5396	41.6
1944	1233	9.6	1583	12.3	404	3.1	1147	8.9	871	6.7	5239	40.5
1945	1139	8.8	1510	11.6	426	3.3	1175	9.1	803	6.2	5053	38.9
1946	1175	8.5	1645	11.8	433	3.1	1409	10.1	870	6.2	5531	39.7
1947	1292	9.0	1816	12.7	580	4.0	1338	9.3	997	6.9	6023	42.0
1948	1171	8.1	1885	12.9	717	4.9	1411	9.6	1052	7.2	6236	42.6
1949	1253	8.5	1750	11.8	692	4.6	1435	9.6	1209	8.1	6339	42.7
1950(1)	1316	8.7	1921	12.7	742	4.9	1655	11.0	1354	9.0	6989	46.3

* From Fats & Oils Situation #148 April 1951, P. 19 as modified
(1) Preliminary
(2) 80.5% used to convert actual weight to fat basis

An examination of this Table shows (1) the relative stability of the per capita consumption of all fats, if we consider the war years abnormal ones, (2) the decrease in butter consumption, (3) the steady per capita consumption of lard, hardly affected by the war period, (4) the steady increase in consumption of margarine, relatively unaffected by the war years and in an amount about sufficient to balance the decrease in butter consumption, (5) the slight drop in per capita shortening consumption, accentuated by war conditions, and (6) the rapid increase of fats for miscellaneous edible uses, such as salad dressings, mayonnaise, etc. Table 10 illustrates points 1 to 6 above.

Table 10

TRENDS INDICATED FROM TABLE 9
in Terms of Annual Per Capital Consumption of Edible Fats
in pounds, for the period 1936 - 1950

	Butter	Lard	Margarine	Shortening	Edible Oil Products	Total
1936	13	11	3	12	6	45
1950	9	13	5	11	9	47
Decrease by	4	-	-	1	-	-5
Increase by		2	2		3	+7

Considering the interpretation given by Fats and Oils Situation #140, P 19, then the slight drop in shortening must be considered as more than compensated for by the decided increase in miscellaneous edible products which for the most part are made from vegetable oils and margarine. The situation in regard to lard itself is stable. Since per capita consumption is relatively stable, any great increased use of animal fats, particularly lard, would have to come through displacement of either butter fat or vegetable oils. The present trend is to use the cheaper and more available lard in shortenings. In pre-war years this amounted to 16 million pounds, by 1949 it had grown to 127 million pounds and in 1950 was 170 million pounds (Fats and Oils Situation #150, July 1951, P12). The use of lard in margarine and other edible products has not been promising to date, either percentage wise or in actual tonnage. The processing of lard to yield a shortening increases its value. This is highly desired by the packer. As more and more lard is used for this purpose, the price should strengthen until a point is reached at which its use in soap or for export would be curtailed. On this basis, the present potential market for lard in shortening would be about 30% or approximately 800 million pounds per year as indicated in Table 11 below.

<div align="center">

Table 11[(1)]

LARD AND RENDERED PORK FAT SUPPLY (MILLIONS OF POUNDS)
AND DISPOSITION IN PER CENT

</div>

Year	Total Disappearance (2)	Export	Percent of Total		
			Used as Lard	Used in [(3)] Edible Products	Used in[(3)] Inedible Products
1936	1586	8.6	91.0	0.4	0.1
1937	1524	10.7	89.1	0.2	0.1
1938	1674	13.9	85.8	0.3	0.1
1939	1979	15.6	84.0	0.4	0.1
1940	2156	10.8	88.1	1.1	0.1
1941	2323	18.3	79.2	2.5	0.1
1942	2491	27.6	69.6	2.8	0.1
1943	2679	29.7	65.1	1.9	3.3
1944	2895	32.4	59.3	1.8	6.5
1945	2393	28.1	67.2	1.3	3.4
1946	2157	22.7	76.2	1.1	0.1
1947	2369	17.7	77.6	4.5	0.2
1948	2349	13.9	80.9	5.0	0.2
1949	2595	25.7	68.4	4.7 (4)	1.2
1950	2649	19.7	70.6	6.4 (4)	3.3

(1) Based on data from Fats and Oils Situation #150, July 1951, Table 8.
(2) Total supply including imports adjusted for stocks.
(3) Split between edible and inedible in proportion to that given in
      Bureau of Census reports for same periods.
(4) Figure of 127 million and 170 million pounds to shortening in 1949
      and 1950, respectively, was used with balance to inedible (prac-
      tically all to soap.)

It is the consensus of lard producers and independent investigators who have
worked with both lard and vegetable oils in shortening manufacture, that lard
may be processed to yield as good a shortening as a vegetable oil. Original-
ly, lard was considered to be the ideal shortening, and when the process of
hydrogenation was first introduced commercially in America, around 1910 or a
little later, the object was to make a product from cottonseed oil or other
edible oil then available, as close as possible to lard in color, texture and
other characteristics. The fact that the product was made from vegetable oil
was not disclosed to avoid prejudice against it by the consumer.

The method used was to hydrogenate the refined and bleached oil to a low iodine
value such as 15 or 20 and then to blend it with unhydrogenated or partially
hydrogenated refined and bleached oil in such proportions that the final product
had a melting point of about 30-35° C. It was later discovered that a product
having superior keeping qualities was made more satisfactorily by slightly hydro-
genating the entire oil to the same melting point. Generally the iodine value
was lowered from about 105-115 to about 65-75. In the first case, the blended
oils still contain about 80% or so of unhardened or partially hardened oil

which contains a high percentage of unsaturates, particularly of linoleic and linolenic glycerides. In the second case, the hydrogenation has a chance, by the selectivity of the process, to remove the highly unsaturated glycerides before large portions are converted into undesired stearates, isooleates and elaidates.

Within a few years, the technical development of vegetable based shortening had grown to a point where it was superior to lard in keeping qualities, texture, uniformity and by the use of emulsifiers, even in shortening properties. Most of these advantages of a vegetable shortening were due to processing. Since the oil required hydrogenation, the process could be adjusted to a point where the melting points could be held within very close limits. Refining and bleaching operations enabled close control of free fatty acids and color, and deodorization gave bland products. Lastly, crystallization operations where the oil was quickly chilled, were developed. The combined effect of several such factors (melting point, air content, chilling methods etc.) permitted very close control of the consistency of the product. Such processing made it possible to prepare products with different specifications to suit varying trade and retail requirements. The term "from purely vegetable oils" became synonymous with quality of product, and hydrogenated vegetable oil shortenings soon commanded a premium price over lard.

Lard lacks natural antioxidants and is less stable than the vegetable oils. Lard also varies in its characteristics (iodine value, melting point and stability) within a fairly wide range depending largely on the methods of rendering, selection of the stock and on the diet of the hog from which the fat is obtained. By proper processing and treatment, however, lard can be converted to as good a product as the hydrogenated vegetable oils in many respects and superior in other.

The principal advantage of lard is that it is a fairly good shortening without recourse to expensive processing and it can be marketed cheaply. This accounts largely for its present extensive use. For example, in a survey covering 1600 families in 68 cities (Home Nutrition and Home Economics of the USDA through Fats & Oils Facts, Am. Meat Institute Sept. 1949 issue, Chart 150), the weekly consumption of lard was from two to four times as high in families with a net income of $1,000, than with those families having a net income of $5,000.

Lard As A Shortening And Margarine Material

The consensus as to the merits of lard as a shortening material seems to be that if properly processed it is as good as a vegetable shortening. Proper processing means to

      (1) stablize it against rancidity

      (2) hydrogenate it to proper consistency

      (3) deodorize it properly

      (4) package it attractively.

Point (1): Stabilization is done by adding any one of the numerous stabilizing agents, such as the alkylated hydroxyanisole synergistic mixture. About 1 pound is used per ton of lard. Other stabilizing agents include dihydroguauretic acid, tannic acid, deodorizer sludge, gum guaiac, or esters of gallic acid. The results of stabilization of lard to date have been very satisfactory and indicate that a solution to this most important problem exists.

Point (2): Lard is not uniform from season to season or geographically. Hence lard had a bad time competing with a hydrogenated vegetable oil whose consistency could be duplicated to a few tenths of a degree centrigrade. By hydrogenating a lard fully and then blending this with an untreated lard the consistency can be made uniform and the product still retains much of the linoleic acid present in the original lard. It is convenient to ship fully hydrogenated lard from a central plant to distant points for blending with the unhydrogenated lard. This saves transportation charges on moving a larger bulk of material and it saves capital expenditure for setting up hydrogenation units at distant plants. This is a very real problem, particularly to small packers. However, experience shows that an all hydrogenated vegetable oil is superior in keeping qualities to a blended product made from full hydrogenated vegetable oil (iodine value 15 to 20) and an unhydrogenated oil, or even with a partially hydrogenated vegetable oil. There is no reason to believe that lard would behave differently. In addition, the benefit of the few per cent linoleic acid remaining in the lard might be offset by the increased stearic acid content of the highly hydrogenated fraction. The solution to this problem probably lies in a more easily controlled and continuous hydrogenation procedure than that which is at present available. It is believed that research along such lines would be of value.

Point (3): Deodorization is a problem with small manufacturers but not with large ones. It is essential to produce a product comparable to a vegetable shortening.

Point (4): Packaging of lard is now being handled with skill by the packers. The shortening value of lard is superior to vegetable products and it requires less creaming in the votator.

An emulsifying agent, such as the monoglycerides of lard, should be incorporated to the extent of a few percent to bring the creaming value up to that of vegetable shortening similarly treated. Since the shortening power of lard is considered to be superior to vegetable shortening the requirement in this respect may be small. It is known that practically all shortenings today do contain emulsifiers which in general are the mono and diglycerides of the oils or fats used in the original products.

In regard to packaging and marketing, several problems appear. The package should be designed to maintain maximum keeping qualities to relieve as much load on the anti-oxidant as possible. Vegetable shortening methods of packaging are worth studying. The use of the term "lard" after the product has been processed appears to offer a handicap to the producers of lard.

PATENTS CONSULTED IN THE SURVEY

Patent No.

1,762,742	W. Reppe (to I. G. Farbenindustrie)
1,913,454	V. R. Kokatnur
1,888,820	A. A. Epstein (to Consolidated Patentees Inc.)
1,991,955	A. W. Ralston (to Armour & Co.)
2,005,619	G. D. Graves (to Du Pont)
2,019,022	N. D. Scott et al. (to Du Pont)
2,033,536	A. W. Ralston et al. (to Armour & Co.)
2,033,537	" " " " " " " " "
2,043,965	K. Smeykal (to I. G. Farbenindustrie)
2,053,045	A. W. Ralston et al. (to Armour & Co.)
2,053,046	A. W. Ralston et al. (to Armour & Co.)
2,054,638	E. Schirm (Deutsche Hydrierwerke A. G.)
2,061,314	A. W. Ralston (to Armour & Co.)
2,078,922	H. R. Arnold (to DuPont)
2,086,690	W. Zerwick et al. (to General Aniline)
2,088,325	J. E. Kirby (to Du Pont)
2,089,212	W. Kritchevsky (to Ninol Corp.)
2,101,314	A. Grun (to Am. Hyalsol Corp.)
2,104,421	A. Grun (Bohme Fettchemie)
2,120,512	E. Rosenhauer (to Henkel & Cie)
2,122,644	J. Harwood (to Armour & Co.)
2,132,388	G. J. Berchet (to Du Pont)
2,132,849	G. H. Greenwalt (to Du Pont)
2,132,902	S. Lenher (to Du Pont)
2,135,327	V. Conquest (to Armour)
2,143,751	H. Adkins (to Rohm & Haas)
2,145,802	A. W. Ralston (to Armour & Co.)
2,145,803	" " " " " " "
2,145,804	" " " " " " "
2,159,967	M. Engelmann (to Du Pont)
2,162,971	A. W. Ralston (to Armour & Co.)
2,166,093	J. Harwood et al. (to Armour & Co.)
2,175,092	A. W. Ralston et al. (to Armour & Co.)
2,175,093	" " " " " " " " "
2,177,407	V. L. Hansley (to Du Pont)
2,177,619	O. Nicodemus et al. (I. S. Faberindustrie)
2,178,139	A. K. Epstein (to Emulsol Corp.)
2,178,522	A. W. Ralston et al. (to Armour & Co.)
2,180,730	H. L. Cox (to Union Carbide & Carbon)
2,187,244	V. Mills (to Procter & Gamble)
2,190,921	B. R. Harris (to Emulsol Corp.)

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Patent No.	
2,191,295	H. Dohse (to I. G. Farbenindustrie)
2,192,664	W. Kritchevsky (to Ninol Inc.)
2,195,573	" " " " " "
2,198,806	A. K. Epstein et al. (to Emulsol Corp.)
2,200,298	E. A. Robinson (to Nat. Oil Prod. Co.)
2,200,390	S. E. Freeman (to Pittsburgh Plate Glass)
2,200,391	" " " " " " "
2,202,826	O. L. Brandes (to Gulf Res. & Dev.)
2,203,641	R. Kapp (to Nat. Oil Prod. Co.)
2,203,642	" " " " " " "
2,205,076	C. G. Wortz (to Du Pont)
2,206,351	R. Greenhalgh (to Imperial Chem.)
2,208,598	G. W. Rigby (to Du Pont)
2,209,383	L. H. Bock (to Rohm & Haas)
2,212,654	W. V. Wirth (to Du Pont)
2,214,254	V. Mills et al. (to Procter & Gamble)
2,219,879	B. M. Vanderbilt (to Commercial Solvents)
2,221,377	B. R. Harris (to Emulsol)
2,221,485	J. E. Kirby et al. (to Du Pont)
2,222,728	F. X. Tartaron (to Phos. Rec. Corp.)
2,224,925	R. H. Potts et al. (to Armour & Co.)
2,224,984	" " " " " " " "
2,224,986	" " " " " " " "
2,227,823	H. L. Cox (to Union Carbide & Carbon)
2,229,307	A. W. Ralston et al. (to Armour & Co.)
2,231,979	E. Wolter (to Procter & Gamble)
2,232,485	J. H. Shipp (to Du Pont)
2,235,098	R. L. Brandt (to Colgate-Palmolive-Peet)
2,235,534	K. L. Russell et al. (to Colgate-Palmolve-Peet)
2,237,729	T. W. Evans et al. (to Shell Dev. Co.)
2,247,711	A. W. Ralston (to Armour & Co.)
2,263,729	W. Hentrich (to Procter & Gamble)
2,266,136	M. Weisberg (to Alrose Chem. Co.)
2,266,591	E. W. Eckey et al. (to Procter & Gamble)
2,267,965	A. W. Wilson (to Carbide & Carbon)
2,271,619	G. B. Bradshaw et al. (to DuPont)
2,274,058	M. T. Goebel et al. (to Du Pont)
2,277,015	H. H. Guest (to J. B. Williams Co.)
2,278,309	S. E. Freeman (to Pittsburgh Plate Glass Co.)
2,278,372	J. F. Olin (to Sharples Chem. Co.)

Patent No.	
2,278,373	J. F. Olin (to Sharples Chem. Co.)
2,279,314	L. F. Henderson et al. (to Lever Bros.)
2,280,850	A. W. Ralston et al. (to Armour & Co.)
2,287,219	H. P. Young et al. (to Armour & Co.)
2,289,044	J. Ross (to Colgate-Palmolive-Peet)
2,291,461	S. E. Freeman (to Pittsburgh Plate Glass Co.)
2,293,676	L. D. Myers et al. (to Emery Ind.)
2,297,864	H. Beck (to Heberlein Pat. Corp.)
2,298,291	H. M. Corley et al. (to Armour & Co.)
2,298,501	L. D. Myers et al. (to Emery Ind.)
2,302,697	M. Katzman (to Emulsol Corp.)
2,304,304	J. H. Fritz (to Nat. Oil Prod.)
2,304,369	W. L. Morgan (to Arnold, Hoffman & Co.)
2,304,830	M. Katzman (to Emulsol Corp.)
2,305,830	E. Profft (to Alien Prop. Custodian)
2,307,047	M. Katzman et al. (to Emulsol Corp.)
2,308,116	I. Silverman (to L. Sonneborn Sons Inc.)
2,313,360	A. W. Ralston et al. (to Armour & Co.)
2,313,636	S. E. Freeman (to Pittsburgh Plate Glass Co.)
2,315,734	A. W. Ralston et al. (to Armour & Co.)
2,316,512	S. E. Freeman (to Pittsburgh Plate Glass Co.)
2,317,301	A. W. Ralston et al. (to Armour & Co.)
2,317,666	A. W. Burwell et al. (to Alox Corp.)
2,320,009	A. W. Ralston et al. (to Armour & Co.)
2,320,010	" " " " " " " " "
2,321,020	E. E. Greger et al. (to Colgate-Palmolive-Peet)
2,322,056	R. H. Potts (to Armour & Co.)
2,325,489	J. T. Easton (to E. F. Houghton & Co.)
2,328,021	M. Katzman (to Emulsol Corp.)
2,329,086	E. A. Robinson et al. (to Nat. Oil Products).
2,329,406	E. A. Mauersberger (to Alframine Corp.)
2,340,343	A. S. Richardson et al. (to Procter & Gamble)
2,340,344	" " " " " " " " "
2,352,160	A. C. Brown (to Emery Ind.)
2,354,719	B. I. Verbeck (to Wilson & Co.)
2,355,314	M. R. McCorkle (to Armour & Co.)
2,355,356	H. P. Young (to Armour & Co.)
2,356,884	A. W. Ralston et al. (to Armour & Co.)
2,356,903	R. C. Wood (to Procter & Gamble)
2,358,776	H. Goldstein (to L. Sonneborn Sons, Inc.)

2,363,047	M. DeGroote (to Petrolite Corp.)
2,363,672	I. L. Jakobsen (to General Mills, Inc.
2,365,290	D. Price et al. (to Nat. Oil Products)
2,365,431	L. Orthner et al. (to Alien Property Custodian)
2,365,915	J. E. Taylor (to Procter & Gamble)
2,366,534	J. E. Kirby (to Du Pont)
2,367,366	J. F. Olin et al (to Sharples Chem. Inc.
2,372,160	R. C. Morris et al. (to Shell Dev. Co.)
2,374,213	M. Katzman (to Emulsol Corp.)
2,377,029	F. A. Norris (to General Mills Inc.)
2,377,030	F. A. Norris (to General Mills Inc.)
2,377,031	" " " ' " " "
2,377,610	L. C. Brown (to Industrial Patents Corp.)
2,381,314	W. H. Shields (to Emery Ind.)
2,383,525	N. B. Tucker (to Procter & Gamble)
2,383,526	N. B. Tucker (to Procter & Gamble
2,383,579	H. D. Allen et al. (to Colgate-Palmolive-Peet
2,383,580	C. J. Arrowsmith et al. (to Colgate-Palmolive-Peet)
2,383,581	" " " " " " " " "
2,383,596	E. E. Dreger (to Colgate-Palmolive-Peet Co.)
2,383,599	G.A. Glossop (to Colgate-Palmolive-Peet Co.)
2,383,601	G. I. Keim (to Colgate-Palmolive-Peet Co.)
2,383,602	G. I. Keim et al. (to Colgate-Palmolive Peet Co.)
2,383,614	J. H. Percy (to Colgate-Palmolive-Peet Co.)
2,383,632	W. R. Trent (" " " " ")
2,383,633	W. R. Trent (" " " " ")
2,383,737	A. S. Richardson (to Procter & Gamble)
2,384,443	J. C. Cowan et al. (to USDA)
2,384,595	C. M. Blair (to Petrolite Corp.)
2,385,849	F. D. Snell et al. (to Chemsearch Corp.)
2,387,537	H. G. Smith et al. (to Gulf Oil Co.
2,388,154	M. Katzman (to Emulsol Corp.)
2,388,400	F. C. Frank (to Socony-Vacuum Oil Co. Inc.)
2,389,191	J. D. Fitzpatrick et al. (to Emery Ind.)
2,390,528	S. E. Freeman (to Pittsburgh Plate Glass Co.)
2,393,202	L. A. Stegemeyer (to Emery Ind.)
2,398,254	N. K. Rosenthal (to Ninol Dev. Co.)
2,400,001	L. D. Grupelli (to National Oil Products)
2,401,756	J. K. Gunther (to Ind. Pats. Corp.)
2,402,526	J. Pikd (to Du Pont)
2,403,293	J. J. Miskel (to National Oil Prod.)
2,408,959	L. A. Stegemeyer (to Emery Ind.)
2,410,096	R. E. Meyer et al. (to Socony-Vacuum Oil Co.)
2,410,788	W. L. Morgon et al. (to Arnold, Hoffman & Co.)
2,410,789	" " " " " " " " " "

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Patent No.	
2,414,393	R. H. Potts (to Armour & Co.)
2,416,552	E. I. Valco (to Richards Chemical Works)
2,421,157	L. D. Meyers et al. (to Emery Ind.)
2,423,232	S. E. Freeman et al. (to Pittsburgh Plate Glass)
2,427,821	J. T. Tindall (to Commercial Solvents Corp.)
2,430,675	C. A. Hempel (to Mathieson Alkali Wks.)
2,430,897	G. R. VanAtta (to USDA)
2,431,760	F. J. Licata (to Nopco Chem. Co.)
2,431,842	E. Stossel et al. (to Mathieson Alkali Works)
2,433,243	H. G. Smith et al. (to Gulf Oil Corp.)
2,435,828	H. H. Guest (to J. B. Williams Co.)
2,435,829	" " " " " " " "
2,437,705	W. J. Paterson (to Lever Bros.)
2,437,706	" " " " " "
2,443,063	D. E. Adelson (to Shell Dev. Co.)
2,443,184	E. W. Colt (to Armour & Co.)
2,444,828	W. Kaplan (to Sun Chem. Corp.)
2,445,892	D. Swern et al. (to USDA)
2,448,602	E. B. Kester (to USDA)
2,450,235	W. P. Gee (to Texaco Devel. Co.)
2,450,611	R. H. Potts (to Armour & Co.)
2,450,612	" " " " " " "
2,450,858	J. D. Fitzpatrick et al. (to Emery Ind.)
2,454,638	J. T. Dickinson et al. (to M. W. Kellogg Co.)
2,455,374	L. H. Libby et al. (to Lever Bros.)
2,457,741	J. R. Shipner (to Cudahy Packing Co.)
2,458,484	D. E. Terry et al. (to General Mills, Inc.)
2,459,054	C. C. Towne (to Texas Co.)
2,459,818	L. F. Henderson (to Lever Bros.)
2,460,772	L. A. Stegemeyer (to Emery Ind.)
2,461,080	M. M. Piskur et al. (to Swift & Co.)
2,461,349	A. W. Ralston et al. (to Armour & Co.)
2,461,495	D. E. Floyd (to General Mills Inc.)
2,462,758	J. D. Malkemus (to Colgate-Palmolive-Peet)
2,464,094	E. M. Meade (to Lankro Chem. Ltd.)
2,467,905	H. J. Passino et al. (to M. W. Kellogg Co.)
2,468,012	A. F. Isbell (to General Mills)
2,468,436	J. D. Fitzpatrick et al. (to Emery Ind.)
2,468,799	N. W. Ziels et al. (to Lever Bros.)
2,473,154	W. Lange et al. (to Procter & Gamble)
2,474,010	L. D. Myers et al (to Emery Ind.)
2,483,099	S. G. Morris et al (USDA)
2,483,253	H. H. Young et al. (to Swift & Co.)
2,489,713	W. M. Leaders (to Swift & Co.)
2,499,984	E. M. Beavers et al. (to Rohm & Haas Co.)

Patent No.

2,505,012   H. T. Spannuth (To Wilson & Co.)

Brit. Pats.

425,927   W. W. Triggs (Rohm & Haas)
467,166   I. G. Farbenindustrie
499,130   "   "   "
506,049   "   "   "
512,022   "   "   "

536,602   Hoffman La Roche
560,448   Warwick Chemical Co.
567,128   E. H. G. Sargent
577,879   Lever Bros.

577,880   Lever Bros.
578,102   "   "
581,799   "   "
582,699   Du Pont
584,939   Procter & Gamble

585,219   Procter & Gamble
585,219   "   "   "
586,799   Du Pont
605,848   "   "

German Pats.

595,173   H. T. Bohme
648,088   I. G. Farbenindustrie

French Pats.
                      Deutsche Hydrierwerke A. G.
783,008   I. G. Farbenindustrie

Swiss Pats.

210,976   Soc. pour l'ind. chim a Bale

Dutch Pats.

51,865   Industrieele Exploitatiemij